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Mesomorphic phase transitions and electro-optical properties of benzyl fluoroalkyl thioether liquid crystalline compounds

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Four series of liquid crystalline (LC) compounds containing benzyl perfluoroalkyl thioether groups (BFT), 4-*n*-alkoxyphenylbenzyl perfluoroalkyl thioethers (*n*O-BBFT-F*m*F), 4-*n*-alkoxyphenylbenzyl perfluoroisoalkyl thioethers (*n*O-BBFT-F*m*IF), 4-*n*-propylcyclohexylbenzyl perfluoroalkyl thioethers (3-C1BFT-F*m*F) and 4-ethylcyclohexyl-3′-fluorobenzyl perfluoroalkyl thioethers (2-C1FBFT-F*m*F), were synthesized and their mesomorphic phase transitions and electro-optical properties investigated. *n*O-BBFT-F*m*F and *n*O-BBFT-F*m*IF have SmA, SmB and CrE phases, while 3-C1BFT-F*m*F and 2-C1FBFT-F*m*F showed a SmB phase. It was found that the appearance of a LC phase and the thermal stability were closely connected with the chemical structures of the rigid core part and the terminal groups. The electro-optical properties were investigated for BFT using ZLI-1132 as nematic solvent. Some of the BFT compounds have a good solubility of 15 wt % in ZLI-1132 and can be used as a component for lowering the refractive anisotropy (Δn) of the host ZLI-1132 solvent.

1. Introduction

Recently, scientific and industrial interest in fluorinated liquid crystalline (LC) compounds as a new class of LC materials has been increasing, especially since the discovery of fluorophenyl compounds such as 1,2-difluoro-4[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]benzene having excellent voltage holding ratios with good electro-optical properties [1–8]. In preceding work [9, 10], we successfully synthesized benzyl fluoroalkyl ether (BFE) derivatives having $-CH_2-O-CH_2-Rf$ (Rf = fluoroalkyl) as the terminal group (structures shown in figure 1), and investigated their mesomorphic properties. The BFE compounds showed layered LC phases, for example the SmB phase in 4-*n*-propylbicyclohexylbenzyl fluoroalkyl ethers (3-C2BFE-*X*), CrE and/or SmA phases in the 4-*n*-alkoxyphenylbenzyl fluoroalkyl ethers (*m*O-BBFE-*X*), and no mesophase in the 4-*n*-alkylcyclohexylbenzyl fluoroalkyl ethers (*m*-C1BFE-*X*). The electro-optical properties of the BFE compounds were measured for solutions in ZLI-1132 nematic solvent. It was found that they have a good solubility of more than 15 wt % in ZLI-1132 and show good electro-optical properties, especially a lowering of the refractive anisotropy (Δn) of ZLI-1132 nematic solvent.

The purpose of this work is to synthesize a new class of benzyl fluoroalkyl thioether derivatives (BFT compounds), whose chemical structures are shown in figure 1 (*b*), and to clarify their mesomorphic phase transitions and electro-optical properties. The mesomorphic and electro-optical properties are discussed in comparison with those of the BFE compounds.

2. Experimental

The BFT compounds were synthesized by nucleophilic substitution of the fluoroiodide with the sodium salts of the corresponding benzyl thioalcohols, as shown in figure 2. As an example, the synthetic procedure for 3O-BBFT-F4F is described below.

A KOH (2.24 g, 0.04 mol)/water (20 ml) solution was mixed with 4-hydroxybiphenyl-4′-carboxylic acid (**I**) (4.28 g, 0.02 mol) dissolved in ethanol (200 ml). To this mixture, 1-bromopropane (3.69 g, 0.03 mol) was added dropwise during refluxing and the mixture was further boiled for 20 h. Then, after adding a further 20 ml of aqueous KOH (2.24 g, 0.04 mol), the reaction mixture

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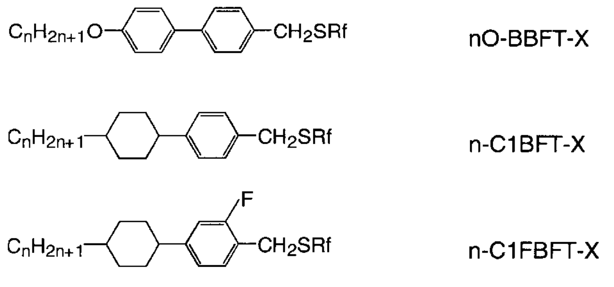
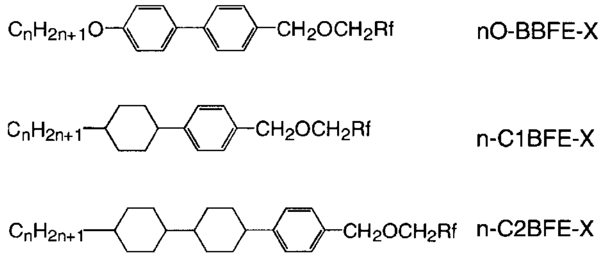


(a) BFT compounds , X (Rf) = fluoroalkyl group and FmF or FmIF (see table 1)



(b) BFE Compounds , X(Rf) = fluoroalkyl group

Figure 1. Chemical structures of (*a*) the benzyl fluoroalkyl thioether (BFT) compounds and (*b*) the benzyl fluoroalkyl ether (BFE) compounds.

was heated at reflux for 2 h. The crude products obtained by evaporating the mixture to dryness were recrystallized from acetic acid and ethanol, giving the compound **II** (white powder, yield 71%). Compound **II** (3.6 g, 0.014 mol) in THF (20 ml) was added dropwise to $LiAlH_4$ (1.3 g, 0.035 mol) in THF (20 ml), and the mixture was heated at reflux for 18 h. The reaction mixture was treated with ethyl acetate and then 3N HCl. The crude compound **III** was obtained by extracting into ethyl acetate. After washing with water, the compound was obtained by evaporation and recrystallization from ethanol (white powder, yield 78%). Thionyl chloride (1 ml) was added to compound **III** (2.7 g, 0.011 mol) in $CHCl_3$ (30 ml) and the mixture stirred at room temperature for 3 h. The crude product obtained was recrystallized from hexane, giving compound **IV** (white powder, yield 95%). 4-*n*-Propoxyphenylbenzyl chloride (**IV**) (2.6 g, 0.010 mol) in acetone/$CHCl_3$ (1/1, 100 ml) was added dropwise to potassium *O*-ethyldithiocarbonate (2.4 g, 0.015 mol) in acetone (50 ml) under N_2, and the mixture stirred for 6 h at room temperature. The reaction product (**V**) was extracted into chloroform and after washing with water, the chloroform solution was evaporated to dryness, giving the crude product **V**. Ethylenediamine (10 ml) was added dropwise under N_2 into a solution of the crude product **V** in chloroform (50 ml). The mixture was stirred at room temperature for 2 h and then poured into chilled 5 wt% aqueous H_2SO_4 (100 ml). The crude product was extracted into chloroform and the extract washed with 5 wt% aqueous H_2SO_4 and then water; it was then evaporated to dryness. The compound **VI** was purified by column chromatography (silica gel, 1:1 benzene/hexane) (white powder, yield 83%).

Finally 3O-BBFT-F4F (**VII**) was synthesized by nucleophilic reaction of 4-*n*-propoxyphenylbenzyl thioalcohol with perfluorobutyl iodide; compound **VI** (1.0 g, 0.004 mol) dissolved in THF (50 ml) was added to NaH (0.19 g, 0.004 mol) in THF (30 ml) under protection of N_2, and the mixture was stirred for 30 min. Perfluorobutyl iodide (2.0 g, 0.006 mol) was added dropwise to the mixture which was then stirred at room temperature for 10 h. After extracting into ethyl ether and then washing with water, the crude product was obtained by evaporating to dryness. The product was

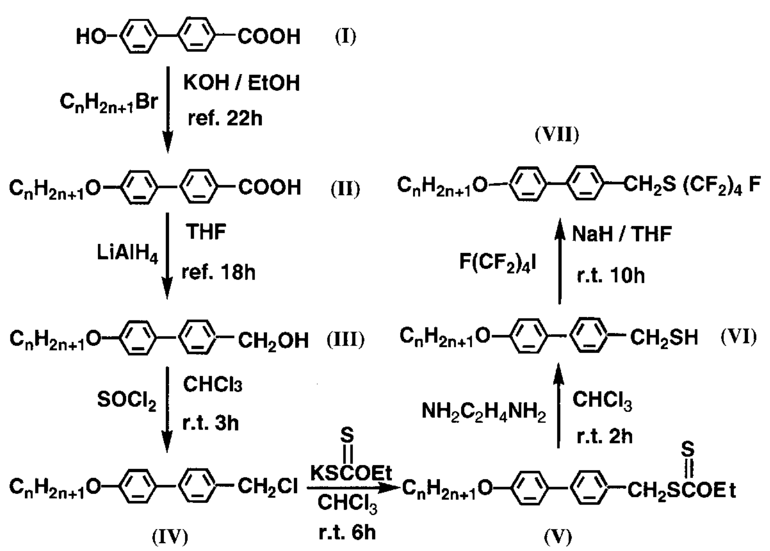


Figure 2. Scheme of synthesis for BFT compounds.

purified by a column chromatography (silica gel, 1 : 1 benzene/hexane) and by further recrystallizations from ethanol, giving compound **VII** (white powder, yield 59%).

1H NMR (400 MHz, $CDCl_3$): δ 1.06 (3H, t, CH_3, $J = 7.4$), 1.83 (2H, m, CH_2), 3.97 (2H, t, CH_2, $J = 6.5$), 4.21 (2H, s, CH_2), 6.96 (2H, d, Ph–H, $J = 8.8$), 7.39 (2H, d, Ph–H, $J = 8.2$), 7.50 (2H, d, Ph–H, $J = 8.8$), 7.53 (2H, d, Ph–H, $J = 8.3$). 19F NMR (400 MHz, $CDCl_3$): δ 68.07, 74.83, 110.08, 114.96 (JEOL FT-NMR 400 MHz). The purity of 3O-BBFT-F4F was judged to be 99.0% by GC.

3-C1BFT-F*m*F and 2-C1FBFT-F*m*F were obtained by almost the same synthetic procedure as described above (figure 2) using 4-propylcyclohexylphenyl-4′-carboxylic acid and 4-ethylcyclohexyl-3′-fluorobenzyl-4′-carboxylic acid as the starting materials, respectively.

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 N_2 flow of 30 ml min^{-1}. Indium and tin were used as the enthalpy standards. The textures of the mesophases were observed using a Nikon Optiphot-Pol polarizing microscope equipped with a Mettler FP-82 hot stage.

The electro-optical properties were measured for the benzyl thioether compounds dissolved in nematic ZLI-1132 at 25°C; the refractive anisotropy (Δn) was measured using an Atago 4T/2T Abbé refractometer, the dielectric anisotropy ($\Delta\varepsilon$) was obtained using a Hewlett Packard 4284A LCR meter, and the viscosity (η) was recorded by a Tokimec ELD-R rotational viscometer.

3. Mesomorphic phase transitions

Figure 3 shows DSC curves for several fluoroalkyl benzyl thioether compounds. The phase transition parameters obtained from the 2nd heating DSC curves are summarized in table 1, where the types of mesophase were determined from the DSC data and polarized microscopic observations. In 3O-BBFT-F6F, four endothermic peaks are observed near 68.2, 88.1, 100.4 and 160.1°C on the 1st heating; these are caused by phase transitions from crystalline (Cr) to crystal E phase (CrE), from CrE to SmB, from SmB to SmA and from SmA to isotropic liquid (I), respectively. On 1st cooling, the I–SmA, SmA–SmB and SmB–CrE phase transitions are also observed near 158.5, 99.9 and 87.7°C, respectively, but the CrE–Cr phase transition is not seen down to room temperature, due to supercooling. The 2nd heating curve shows an exothermic peak near 62.1°C due to recrystallization, and then repeats the 1st heating curve. The type of mesophase was determined by texture observations using crossed polarizers and optical microscopy. A focal-conic fan SmA texture and a fan-shaped SmB texture with a diminished number of discontinuities were seen in the temperature ranges from 158.5 to 99.9 and to 87.7°C, respectively, on cooling; then tie lines (transition bars) appeared on the fan texture from 87.7°C, which indicated the appearance of the CrE phase [11]. Consequently it was concluded that 3O-BBFT-F6F undergoes Cr ⇔ CrE ⇔ SmB ⇔ SmA ⇔ I phase transitions. The phase transition sequences for the other *n*O-BBFT-F*m*F were determined in almost the same way as those for 3O-BBFT-F6F. 3O- and 5O-BBFT-F4F showed Cr ⇔ CrE ⇔ SmA ⇔ I phase transitions but did not have the SmB phase, while 3O-BBFT-F8F showed only a SmA phase on heating but formed a monotropic CrE phase on cooling; this apparently results from the high melting temperature (106.3°C).

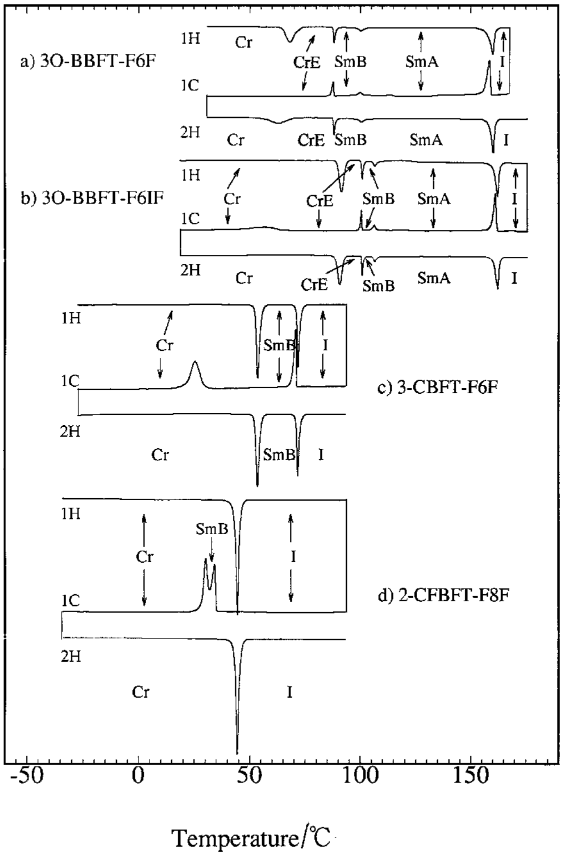
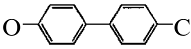
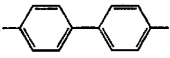
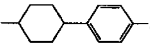
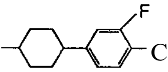


Figure 3. DSC thermograms for typical BFT compounds.

The phase transition behaviour was also measured for the 3O-BBFT-F*m*IF having a CF_3 branch at the terminal fluoroalkyl group. The DSC curves are shown for 3O-BBFT-F6IF as an example in figure 3 (*b*). Apparently, 3O-BBFT-F6IF shows enantiotropic Cr ⇔ CrE ⇔ SmB ⇔ SmA ⇔ I phase transitions, similarly to 3O-BBFT-F6F. Phase transition parameters are listed in table 1 for all the *n*O-BBFT-F*m*IF compounds studied here. 3O-BBFT-F4IF shows CrE and SmA

Table 1. Phase transition temperatures (°C) and associated enthalpy changes (kJ mol^{-1}, in brackets) for the benzyl perfluoroalkyl thioether (BFT) derivatives. ● = enantiotropic phase transition, ▲ and [] = monotropic phase transition.

Compounds	Terminal groups	Cr		CrE		SmB		SmA		I
nO-BBFT-FmF	$(C_nH_{2n+1}O$  $CH_2S(CF_2)_mF)$									
3O-BBFT-F4F	$-(CF_2)_4F$	●	85.7 (2.3)	●	94.5 (1.3)			●	140.1 (8.4)	●
5O-BBFT-F4F	$-(CF_2)_4F$	●	47.1 (7.3)	●	77.0 (4.5)			●	118.5 (7.4)	●
3O-BBFT-F6F	$-(CF_2)_6F$	●	68.2 (7.5)	●	88.1 (2.4)	●	100.4 (2.1)	●	160.1 (10.8)	●
3O-BBFT-F8F	$-(CF_2)_8F$	●	106.3 (20.0)	▲	[101.5] [(1.1)]			●	172.8 (10.9)	●
nO-BBFT-FmIF	$(C_nH_{2n+1}O$  $CH_2S(CF_2)_pCF(CF_3)_2$, m = p + 2)									
3O-BBIFT-F4IF	$-(CF_2)_2CF(CF_3)_2$	●	70.9 (6.3)	●	97.5 (4.2)			●	135.1	●
5O-BBFT-F4IF	$-(CF_2)_2CF(CF_3)_2$	●	71.9 (12.9)					●	115.3 (1.2)	●
3O-BBFT-F6IF	$-(CF_2)_4CF(CF_3)_2$	●	91.4 (13.1)	●	100.8 (0.8)	●	106.5 (1.6)	●	162.3 (11.4)	●
3O-BBFT-F8IF	$-(CF_2)_6CF(CF_3)_2$	●	95.3 (15.2)	●	98.6 (3)	●	106.9 (1.5)	●	172.7 (11.8)	●
3-C1BFT-FmF	$(C_3H_7$  $CH_2S(CF_2)_mF)$									
3-C1BFT-F4F	$-(CF_2)_4F$	●	29.6 (13.1)			●			39.0 (8.1)	●
3-C1BFT-F6F	$-(CF_2)_6F$	●	53.5 (22.3)			●			71.8 (13.2)	●
3-C1BFT-F8F	$-(CF_2)_8F$	●	85.4 (21.8)			●			93.0 (12.7)	●
2-C1FBFT-FmF	$(C_2H_5$  $CH_2S(CF_2)_mF)$									
2-C1FBFT-F4F	$-(CF_2)_4F$	●	− 26.1 (15.3)							●
2-C1FBFT-F6F	$-(CF_2)_6F$	●	6.2 (11.6)			▲			[− 10.2] [(1.7)]	●
2-C1FBFT-F8F	$-(CF_2)_8F$	●	44.5 (41.5)			▲			[30.4] [(8.4)]	●

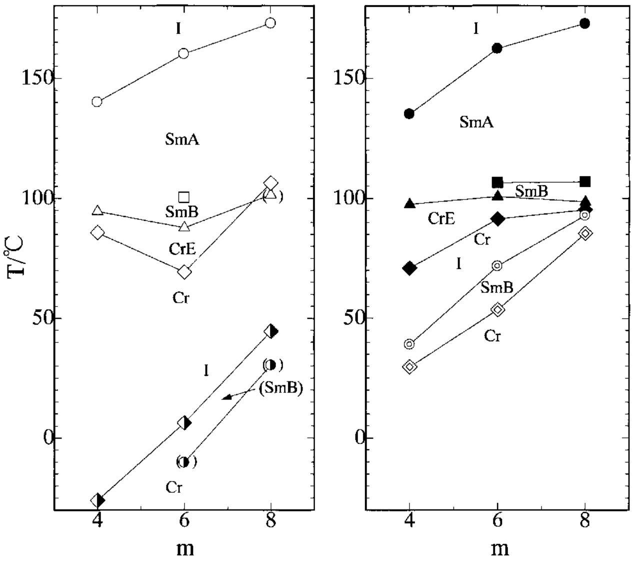
phases between 70.9 and 97.5°C, and 97.5 and 135.1°C, respectively, but 5O-BBFT-F4IF has only a SmA phase between 71.9 and 115.3°C. Both 3O-BBFT-F6IF and -F8IF compounds with longer fluoroalkyl group show CrE, SmB and SmA phases, similarly to those for *m*O-BBFT-F*m*F.

DSC curves for 3-C1BFT-F6F are shown in figure 3(*c*). An enantiotropic SmB phase is shown between 53.5 and 71.8°C on the 1st heating and between 70.6 and 25.8°C on the 1st cooling. The appearance of an enantiotropic SmB phase is also seen in other 3-C1BFT-F*m*F compounds as shown in table 1. The SmB phase was identified by a polarizing optical microscopic observations: a typical mosaic texture with doubly refracting lancets and pseudo-isotropic regions were observed below 70.6°C on cooling from the I phase [11].

Figure 3(*d*) shows DSC curves for 2C1FBFT-F8F. A melting transition from crystalline (Cr) to the isotropic liquid phase (I) was observed at 44.5°C on the 1st heating, while on the 1st cooling, the SmB phase was observed monotropically between 33.9 and 30.4°C. As shown in table 1, the monotropic SmB phase was also seen in 2C1FBFT-F6F, but not in 2C1FBFT-F4F which showed no mesophase.

Consequently, the mesogenicity of the BFT compounds is closely connected with the chemical structures of the rigid core parts and terminal groups. *n*O-BBFT-F*m*F and *n*O-BBFT-F*m*IF compounds having the biphenyl group as the rigid core part tend to generate CrE, SmB and SmA phases, while 3-C1BFT-F*m*F and 2-C1FBFT-F*m*F preferentially form the SmB phase. However, the mesophase thermal stability in the 3-C1BFT-F*m*F compounds is much lower than that in the BBFT compounds (the clearing point is much lower in the 3-C1BFT-F*m*F than in the BBFT). In the 2-C1FBFT-F*m*F, the SmB phase is monotropic in 2-C1FBFT-F6F and -F8F and is not seen in 2-C1FBFT-F4F, which is clearly caused by the broadening of the molecule by the F-substitution in the benzene core. These effects may also be caused by the more flexible cyclohexylbenzyl core compared with the biphenyl core part. Figure 4 shows plots of the phase transition temperatures versus the length of the fluoroalkyl terminal group (*m*) in $-CH_2-S-(CF_2)_mF$ and $-CH_2-S-(CF_2)_pCF(CF_3)_2$ ($m = p + 2$). Apparently the length of the fluoroalkyl terminal group (*m*) strongly influences the mesomorphic properties. In all the BFT compounds the clearing point increases proportionally to *m*, which may be explained by the rigidity of the fluoroalkyl terminal group. It is noted that the clearing point for *n*O-BBFT-F*m*F is nearly equal to that for *n*O-BBFT-F*m*IF bearing a $-CF_3$ branch.

As mentioned in the Introduction, we previously reported the mesogenicity for three series of benzyl fluoroalkyl ether derivatives (BFE compounds, see figure 1), *m*O-BBFE-*X*, *m*C1BFE-*X* and 3-C2BFE-*X*. The mesomorphic phase transition behaviour was again closely connected with the chemical structure, similarly to the BFT compounds in this work; 3O-BBFE-*X* shows SmA and/or CrE, and 3-C2BFE-*X* generates a SmB phase, but *m*C1BFE-*X* shows no mesophase. These results were readily explained by the chemical structures—the rigidity and length of the core part and the fluoroalkyl terminal groups (*Rf*). The BFT and BFE compounds have $-CH_2-S-Rf$ and $-CH_2-O-CH_2Rf$ as the terminal groups, respectively, and it is interesting to see how this difference in the terminal group affects the mesogenicity. The clearing point was 93.6°C for 3O-BBFE-F2F and 61.6, 78.6, 96.0 and 111.8°C for $m = 2$, 4, 6 and 8 of 3O-BBFE-F*m*H having the terminal group $-CH_2-O-CH_2(CF_2)_mH$, while in 3O-BBFT-F*m*F having $-CH_2-S-(CF_2)_mF$, the clearing point changes from 140.1 to 172.8°C on increasing *m* from 4 to 8 as seen in table 1. Therefore, the thermal stability appears to be enhanced by the replacement of $-CH_2-O-CH_2Rf$ by $-CH_2-S-Rf$.



(a) (b)

Figure 4. Phase transition temperatures (*T*) versus the length of the terminal perfluoroalkyl chain (*m*) for (*a*) 3O-BBFT-F*m*F (open symbols) and 2-C1FBFT-F*m*F (half-closed symbols), and (*b*) 3O-BBFT-F*m*IF (closed symbols) and 3-C1BFT-F*m*F (concentric symbols).

4. Electro-optical properties

In preceding papers [9, 10], we have investigated the electro-optical properties of several BFE compounds dissolved in ZLI-1132 as a nematic solvent—for example, 3-C1BFE-PF having $-CH_2OCH_2CF(CF_3)O(CF_2)_2CF_3$ (PF) as the terminal group, 2-C2BFE-F1F and -F2F having terminal groups $-CH_2OCH_2(CF_2)F$ and $-CH_2OCH_2(CF_2)_2F$, respectively, 3-C2BFE-F2H having the terminal group $-CH_2OCH_2(CF_2)_2H$, and 3O-BBFE-PF. These BFE compounds showed a good solubility of more than 15 wt % in ZLI-1132, and lowered the refractive anisotropy (Δn) from 0.137 for ZLI-1132 to 0.116–0.129 by adding 15 wt % of the BFE component, the other electro-optical properties of ZLI-1132 remaining good.

In the present work, we have investigated the electro-optical properties for several BFT compounds in nematic ZLI-1132 solvent, and the data are listed in table 2. The solubility of these compounds in ZLI-1132 is lower, compared with the BFE compounds, reaching 15 wt % only for 3-C1BFT-F4F and 2-C1FBFT-F4F. This low solubility may result from the longer fluoroalkyl terminal group and perhaps the $-CH_2-S-CF_2-$bond of the terminal group. The values of Δn for 15 wt % 3-C1BFT-F4F/ and 15 wt % 2-C1FBFT-F4F/ZLI-1132 solutions are comparable to those for 15 wt % solutions of BFE compounds. Figure 5 shows plots of Δn versus F content in the molecule for 15 wt % BFE or BFT/ZLI-1132 nematic mixtures. The value of Δn decreases almost in proportion as the F content increases, which confirms that F atoms play an importent role in lowering Δn; the longer fluoroalkyl side chains would decrease Δn more, due to the F atoms stacked along the molecular long

Table 2. Electro-optical data for benzyl perfluoroalkyl thioether (BFT) compounds in ZLI-1132 nematic solvent. * T_{NI} = phase transition temperature from nematic phase to isotropic phase. $\Delta\varepsilon$ = dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$; $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants 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 indices, respectively). η = viscosity at 20°C.

Compound	Solubility/wt %	T_{NI}/°C	$\Delta\varepsilon$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	Δn	n_o	n_e	η/mPa s
ZLI-1132		71.7	11.0	15.5	4.5	0.137	1.492	1.629	26.6
3O-BBFT-F4F	10	65.5	10.8	15.3	4.5	0.137	1.490	1.624	28.1
3O-BBFT-F6F	3	70.9	11.2	15.7	4.5	0.137	1.490	1.628	27.8
3O-BBFT-F8F	0								
5O-BBFT-F4F	10	65.5	10.4	14.9	4.5	0.133	1.490	1.623	28.8
3O-BBFT-F4IF	5	66.1	10.8	15.3	4.5	0.133	1.492	1.624	28.5
3-C1BFT-F4F	15	58.4	10.0	14.5	4.5	0.123	1.486	1.609	26.4
2-C1FBFT-F4F	15	50.4	9.8	14.7	4.9	0.117	1.487	1.604	27.4
2-C1FBFT-F8F	10	66.4	10.7	15.2	4.5	0.130	1.486	1.616	28.4

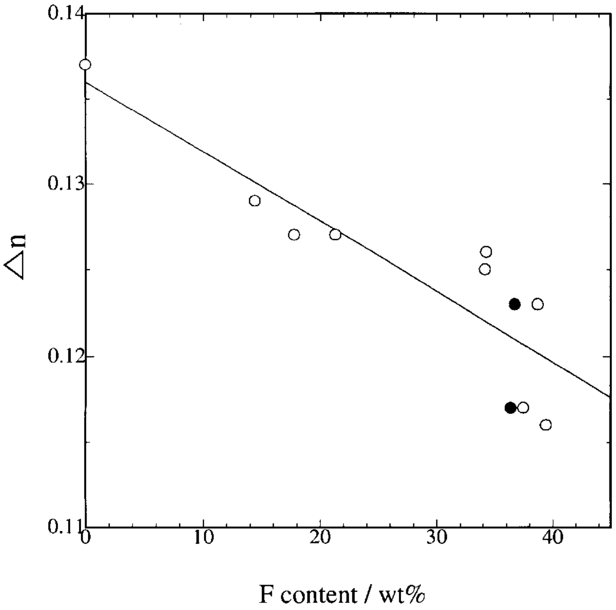


Figure 5. Plots of refractive anisotropy (Δn) of 15 wt % BFT and 15 wt % BFE solutions in nematic ZLI-1132 versus the content of fluorine (wt %) in a molecule. BFT: closed-symbol, BFE: open-symbol.

axis. Consequently, these results indicate that some of these BFT compounds can be used as a component for decreasing birefringence in nematics for LC display devices.

5. Summary

In this work we synthesized a new class of liquid crystalline benzyl perfluoroalkyl thioether (BFT) derivatives and investigated their mesomorphic phase transitions and electro-optical properties. The mesogenicity was closely connected with the chemical structure: *n*O-BBFT-F*m*F and *n*O-BBFT-F*m*IF compounds having a biphenyl group as the core part showed layered mesophases such as SmA, SmB and CrE with good thermal stability; 3-C1BFT-F*m*F having a cyclohexylphenyl group as the core part generated the SmB phase, while 2-C1FBFT-F*m*F having F-substitution in the cyclohexylphenyl core part showed monotropic SmB mesophases. The terminal group also affected the thermal stability of the mesophase significantly. As the terminal group is lengthened, the clearing point is raised because of the rigidity of the perfluoroalkyl groups.

The electro-optical properties were studied for BFT compounds containing the benzyl perfluoroalkyl thioether group, using ZLI-1132 as a nematic solvent. We found that two of the BFT compounds (3-C1BFT-F4F or 2-C1FBFT-F4F) can be used as one component to lower the refractive anisotropy of the host ZLI-1132 nematic solvent.

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