Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Yang, Xiaotun , Abe, Kazuki , Kato, Ryuji , Yano, Shinichi , Kato, Takashi , Miyazawa, Kazutoshi and Takeuchi, Hiroyuki(1998) 'Preliminary communication Electro-optical properties of benzyl fluoroalkyl ether derivatives', Liquid Crystals, 25: 5, 639 — 641

To link to this Article: DOI: 10.1080/026782998205930

URL: http://dx.doi.org/10.1080/026782998205930

LIQUID CRYSTALS, 1998, VOL. 25, NO. 5, 639–641

Preliminary communication

Electro-optical properties of benzyl fluoroalkyl ether derivatives

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(*Received 8 May 1998; in final form 23 June 1998; accepted 28 June 1998*)

Several new fluorinated liquid crystal compounds, 4-*n*-propylbicyclohexylbenzyl fluoroalkyl ethers (C2BFE) and a 4-*n*-propylcyclohexylbenzyl 2-perfluoropropoxy-2,3,3,3-tetrafluoropropyl ether (C1BFE), were synthesized and their phase transition behaviours and electro-optical properties investigated by DSC, polarizing optical microscopy, Abbé refractometry and other physical methods. All the C2BFE compounds showed a layered mesophase like SmB, while C2BFE had no mesophase. All the fluorinated compounds have good solubility in ZLI-1132 (more than 15 wt %) and can be used as a component for lowering the refractive anisotropy (Δn) of the nematic solvent ZLI-1132.

In recent years, scientific and industrial interest has been increasing concerning liquid crystalline (LC) fluorinated compounds, especially since the discovery of 3,4-difluorophenyl compounds such as 1,2-difluoro-4-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]benzene which shows excellent electro-optical properties for LC displays [1–4]. Other LC compounds containing fluoroalkyl or fluoroalkoxy groups as terminal groups have also been studied and these studies are certainly an important way to discover new phenomena and/or LC materials with good electro-optical properties. The $-CF_3$ and $-OCF_3$ terminal groups are known to give a large dipole moment along the molecular long axis and to generate some good electro-optical properties [5–7].

The present work was aimed at investigating the mesomorphic phase transitions and electro-optical properties of 4-*n*-propylbicyclohexylbenzyl fluoroalkyl ethers (C2BFE) and a 4-*n*-propylcyclohexylbenzyl fluoroalkyl ether (C1BFE), all newly synthesized. We report that the C2BFE and C1BFE compounds can act as a component for lowering the refractive anisotropy (birefringence) of ZLI-1132, an important nematic solvent.

4-*n*-Propylbicyclohexylbenzyl chloride was prepared by the following conventional synthetic procedure: 4-*n*-propylbicyclohexylbenzyl alcohol was obtained by reducing ethyl 4-*n*-propylbicyclohexylbenzoate with $LiAlH_4$ and 4-*n*-propylbicyclohexylbenzyl chloride was prepared by a treatment of the alcohol with thionyl chloride.

The C2BFE compounds were synthesized by reaction of 4-*n*-propylbicyclohexylbenzyl chloride obtained as above with the fluoroalkanol; the fluoroalkanol (0·022 mol) was added to a NaH (0·018 mol)/dry ethanol (20 ml) solution and stirred for 1 h. The mixture obtained was heated under reflux with 4-*n*-propylbicyclohexylbenzyl chloride (0·01 mol) for 16 h. The crude product was obtained by extracting into diethyl ether followed by column chromatography (silica gel, 1/1 benzene/hexane). The product was fully purified by recrystallizations from hexane giving colourless crystals (yield: 61·7% for 4-*n*-propylbicyclohexylbenzyl 2,2,3,3-tetrafluoropropyl ether, for example). The compounds were shown to be pure by ^{1}H NMR, ^{19}F NMR (JEOL FT-NMR 400 MHz) and elemental analysis.

For example in the case of 4-*n*-propylbicyclohexylbenzyl 2,2,3,3-tetrafluoropropyl ether: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0{\cdot}88$ (t, 3H, CH_3, $J = 7{\cdot}31$ Hz), 1·75 (2H, m, CH_2), 3·81 (t, 2H, CH_2, $J = 12{\cdot}56$ Hz), 4·59 (s, 2H, CH_2), 7·20 (d, 2H, Ph-H, $J = 8{\cdot}54$ Hz), 7·23 (d, 2H, Ph-H, $J = 9{\cdot}30$ Hz). ^{19}F NMR (400 MHz, $CDCl_3$): $\delta = 79{\cdot}91$, 95·15, 95·30, 110·00. Elemental analysis: calculated for $C_{25}H_{36}OF_4$ C 70·09, H 8·41; found C 70·06, H 8·51%.

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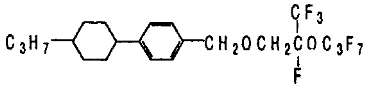
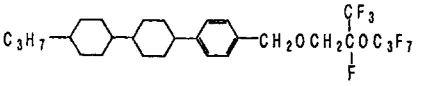
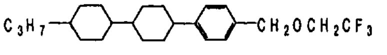
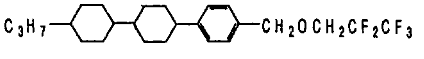
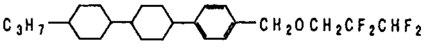
Phase transition temperatures were measured using differential scanning calorimetry (Seiko Denshi DSC-210, SSC-5000 system) at a scanning rate of 5 K min^{-1} and under a dry nitrogen flow of 30 ml min^{-1}. Indium and tin were used as the enthalpy standards. The textures of the mesophase were examined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

The electro-optical properties were measured for 15 wt % of C1BFE or a C2BFE in ZLI-1132. The refractive anisotropy (Δn) was measured by an ATAGO 4T and 2T Abbé refractometer at 25°C, the dielectric anisotropy ($\Delta\varepsilon$) was obtained by using a HEWLETT PACKARD 4284A LCR meter at 25°C, and the viscosity (η) was recorded by employing a TOKIMEC ELD-R rotational viscometer.

Phase transition temperatures and corresponding enthalpy changes are listed for all the compounds used here in table 1. The textures of the LC states were determined by optical microscopy using crossed polarizers: on cooling from the isotropic phase, the C2BFE compounds exhibited a mosaic texture with doubly refracting lancets and pseudo-isotropic regions which may be assigned to a SmB phase [8], but C1BFE gave no mesophase. C2BFE-1, having a branched fluoroalkyl ether chain, shows only a monotropic mesophase like SmB, but the C2BFE materials having *n*-fluoroalkyl ether groups show a mesophase like SmB over a wide temperature range. The values of ΔH for the SmB transitions are between 8·2 and 10·1 kJ mol^{-1} for the C2BFE compounds, values which are somewhat low, but comparable to values reported for compounds such as bis(4-heptylcyclohexyl)-1,4-cyclohexane, 17·57 kJ mol^{-1} [9] and 4′-octyloxy-*N*-[(2-thienyl)methylidene]-4-aminobiphenyl, 16·52 kJ mol^{-1} [10]. The melting enthalpies for the C2BFE are between 10·2 and 28·2 kJ mol^{-1}.

Table 2 shows the electro-optical properties of 15 wt % of C1BFE or a C2BFE compound in ZLI-1132. The values of the dielectric anisotropy ($\Delta\varepsilon$) decrease and of the viscosity (η) increase somewhat with the addition of

Table 1. Phase transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) of the benzyl fluoroalkyl ethers.

Compound	Structure	Cr		SmB		I
C1BFE		•	−69·8			•
C2BFE-1		•	146·4 10·2	•	(144·5)[a] (8·2)	•
C2BFE-2		•	32·1 23·7	•	167·4 10·1	•
C2BFE-3		•	36·5 22·4	•	160·6 8·4	•
C2BFE-4		•	34·0 28·2	•	148·7 8·8	•

[a] ( ) Denotes monotropic phase transition.

Table 2. Electro-optical data for 15 wt % of each of the benzyl fluoroalkyl ethers in ZLI-1132. T_{NI} = phase transition temperature from nematic phase to isotropic phase (°C); $\Delta\varepsilon$ = dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp}$, $\varepsilon_{//}$ 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	T_{NI}	$\Delta\varepsilon$	$\varepsilon_{//}$	$\varepsilon_{\perp}$	Δn	n_o	n_e	η
ZLI-1132	71·7	11·0	15·5	4·5	0·137	1·492	1·629	26·6
C1BFE	47·8	8·9	13·6	4·7	0·116	1·484	1·600	29·4
C2BFE-1	67·7	9·9	14·5	4·6	0·125	1·484	1·609	—
C2BFE-2	74·2	10·0	14·5	4·5	0·129	1·490	1·619	27·2
C2BFE-3	70·7	9·9	14·5	4·6	0·127	1·488	1·615	28·5
C2BFE-4	70·1	10·0	14·7	4·7	0·127	1·490	1·617	30·7

the compounds C1BFE and C2BFE and the nematic–isotropic phase transition temperature (T_{NI}) decreases markedly with the addition of C1BFE. It is noted that all the compounds have a solubility of more than 15 wt % in ZLI-1132 as solvent and obviously decrease the value of the refractive anisotropy (Δn). These results strongly indicate that the C1BFE and C2BFE compounds can be used as a component to decrease the birefringence in nematics for LC display devices.

In conclusion, several new liquid crystalline benzyl fluoroalkyl ethers, C1BFE and C2BFE, have been synthesized. The C2BFE compounds show a mesophase like SmB over a wide temperature range, while C1BFE shows no mesophase. All the benzyl fluoroalkyl ethers used here have a good solubility >15 wt % in ZLI-1132 and can act as a component for lowering the refractive anisotropy (Δn) in ZLI-1132 as nematic solvent.

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