

Liquid-Crystalline Properties of Alkyl 4-[2-(Perfluorooctyl)ethoxy]benzoates

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This paper describes the liquid-crystalline properties of alkyl 4-[2-(perfluorooctyl)ethoxy]benzoates (**1**) and bromo (**2**) and nitro (**3**) substituted compounds. For **1**, the lower members show a smectic A phase; also the smectic A-isotropic transition temperatures and the latent heats decrease with increasing the carbon number of the hydrocarbon chain. An X-ray examination indicated that the smectic A phase has an interdigitated arrangement of molecules. The results are discussed in terms of inter- and intra-layer fluorophilic interactions around the perfluorooctyl groups.

There are many liquid-crystalline materials having a fluoroalkyl group at the terminal position.^{1,2} Generally, the terminal perfluoroalkyl group enhances not only the melting point, but also the mesophase thermal stability. Especially, the perfluoroalkyl group facilitates the formation of smectic phases.³ For example, many liquid crystals having a trifluoromethyl or a trifluoromethoxy group tend to show only the smectic phase, even in the earlier members.^{4–6} In an earlier paper, we also described that some benzene compounds having a perfluoroalkyl group show a smectic phase, while the liquid-crystalline core consists of one benzene ring.⁷

In polymer systems some perfluoroalkyl compounds having no rigid liquid-crystalline core are known to show smectic phases.⁸

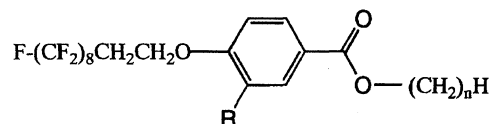
The fluoroalkyl chain is known to be more rigid than the corresponding alkyl one. In addition, strong electrostatic interactions, such as fluorophobic and fluorophilic interactions around the perfluoroalkyl groups, are expected to facilitate the layer arrangement of molecules. Therefore, the perfluoroalkyl group is preferable for one component of liquid-crystalline molecules, and is considered to have the potential to develop new liquid-crystalline materials.

However, the effect of the fluoromethylene chain on layer formation has not been clarified.

In this paper we describe interesting liquid-crystalline properties of some alkyl benzoate derivatives having a 2-(perfluorooctyl)ethoxy group, as shown below (Chart 1). The structural characteristics of the molecules are that the small liquid-crystalline core involves hydrocarbon and perfluoroalkyl chains having very different physical properties. The mesomorphic properties are discussed in terms of the geometrical and electrostatic natures of the perfluoroalkyl group.

Experimental

Materials. Ethyl 4-[2-(Perfluorooctyl)ethoxy]benzoates



Compounds **1** R = H
2 R = Br
3 R = NO₂

Chart 1.

(1b): **1b** was prepared according to the Mitsunobu reaction.⁹ A solution of triphenylphosphine (0.69 g, 2.6 mmol) and 2-(perfluorooctyl)ethanol (1.0 g, 2.0 mmol) in dry THF (10 ml) was added to a solution of ethyl 4-hydroxybenzoate (0.4 g, 2.6 mmol) and diethyl azodicarboxylate (0.46 g, 2.6 mmol) in dry THF (10 ml) at room temperature.⁶ After stirring the mixture overnight at room temperature, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel. The first eluent was recrystallized from methanol to give ethyl 4-[2-(perfluorooctyl)ethoxy]benzoate (**1b**) as colorless needles, 0.155 g (12%). IR: $\nu = 1701$ (C=O) cm^{-1} . ¹H NMR $\delta = 1.38$ (3H, t, $J = 7.1$ Hz), 2.66 (2H, t, $J = 18.3, 6.8$ Hz), 4.33 (2H, t, $J = 6.8$ Hz), 4.34 (2H, t, $J = 7.1$ Hz), 6.92 (2H, d, $J = 8.9$ Hz), and 8.01 (2H, d, $J = 8.9$ Hz). The other homologs were prepared similarly.

Method. IR spectroscopy was performed on a Horiba FT-200 infrared spectrometer. The ¹H NMR spectra were taken with a Nihon-Denshi EX-270 spectrometer in a chloroform-*d* solution, where TMS was used as an internal standard. The transition temperatures and latent heats were determined by using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp 156.6 °C, 28.4 J g⁻¹). The DSC thermogram was operated at a heating rate of 5 °C min⁻¹. The mesophases were characterized by using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). A homogeneous alignment between two glass plates was achieved by treating the of glass surfaces with polyimide (Tore SP-810). A homeotropic alignment was achieved by treating the glass surfaces with cetyltrimethylammonium bromide. X-Ray diffraction experiments were performed using a Rigaku-denki RINT 2200 diffractometer. The reflection

angle was calibrated by a comparison of both the right and left angles. The temperature was controlled by a Rigaku PTC-20A thermo-controller. After a powdered sample crammed into a quartz capillary (1.5 mm Φ) was heated to the isotropic temperature, a measurement was carried out on the cooling process.

Results and Discussion

Thermal Properties: The transition temperatures and latent heats obtained by a DSC thermogram are summarized in Table 1. The thermal data for the melting phenomenon were obtained from the first heating process of the crystals obtained by recrystallization from methanol. The monotropic smectic-isotropic transition data were obtained from the second heating process.

The methoxy compound (**1a**) shows an endotherm at 86 °C corresponding to the melting phenomenon on the first heating process. The molten material showed a small exotherm at 82 °C due to a phase transition during the cooling process. The formed texture is shown in Fig. 1. The mesophase shows a typical focal conic fan texture (Fig. 1), which disappears at 84 °C. We assume that the mesophase has an orthogonal arrangement of molecules, since the mesophase shows the typical focal conic fan texture under a homogeneous alignment, and a typical homeotropic texture (dark under a cross-polarized microscope) under a homeotropic one.

The latent heats for both the melting and smectic-isotropic (S-I) transition tend to reduce with increasing the hydrocarbon chain. Usually, the latent heat for the S-I transition tends to increase with increasing the hydrocarbon chain, since the short-range interaction around the hydrocarbon chains is a function of the alkyl chain length. The present results are opposite to the general trend. The transition temperatures are plotted against the carbon number in Fig. 2.

The melting points tend to decrease with increasing the carbon number of the hydrocarbon chain. This trend may be observed in the usual liquid-crystalline materials. The S-I transition temperatures, interestingly, are steeply reduced with increasing the carbon number of the hydrocarbon chain, and the hexyl homolog (**1f**) does not show any mesophase, even during a rapid cooling process. Usually, the smectic properties are known to be facilitated by a short-range in-

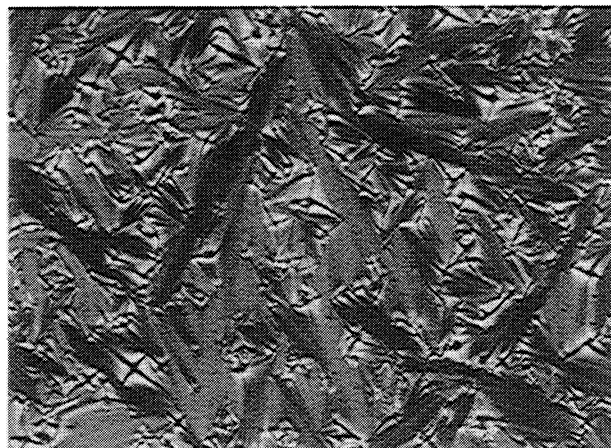


Fig. 1. Micrograph for **1a** at 62 °C (homogeneous alignment, 100 \times).

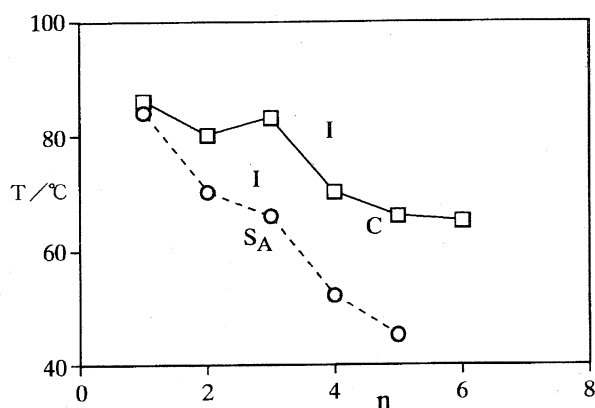


Fig. 2. Plot of transition temperatures against the carbon number of the hydrocarbon chain for **1**. C, S_A, and I indicate crystal, smectic A, and isotropic phases, respectively. The dashed line indicates a monotropic transition.

teraction around the hydrocarbon chains, so that the smectic thermal stability increases with elongating the hydrocarbon chain. Apparently, the feature in the figure is opposite to the general trend. In addition, a plot of the S-I transition temperatures vs. the carbon number shows a weak even-odd effect.

Table 1. Transition Temperatures and Latent Heats for **1**–**3**

Compounds	<i>n</i>	R	Transition temperatures (<i>T</i> /°C)				Latent heats (kJ mol ⁻¹)	
			C	S _A		I	Δ <i>H</i> _{C-I}	Δ <i>H</i> _{S_A-I}
1a	1	H	•	86	(• 84)	•	41.3	5.6
1b	2		•	80	(• 70)	•	50.2	5.1
1c	3		•	83	(• 66)	•	42.6	5.1
1d	4		•	70	(• 52)	•	38.7	4.4
1e	5		•	66	(• 45)	•	33.0	4.1
1f	6		•	65	—	•	34.2	
2a	1	Br	•	82	(• 80)	•	43.1	3.4
2b	2		•	73	(• 56)	•	35.1	2.6
3a	1	NO ₂	•	87	(• 86)	•	32.3	2.4
3b	2		•	95	(• 81)	•	41.0	3.3

C, S_A, and I indicate crystal, smectic A, and isotropic phases, respectively. Parentheses indicate a monotropic transition temperature.

In the present systems, any other smectic phase, such as smectic B and C phases, could not be detected, even in a rapid cooling process.

Thus, compounds **1** have some abnormal thermal properties compared with those of the usual liquid crystals.

X-Ray Diffraction Studies: X-Ray profiles for compounds, **1a**, **1b**, and **1c**, are shown in Fig. 3.

Figure 3(a) shows the profile for **1a** (at 75 °C ($T_{SA-I}-9$ °C)), where a weak reflection at $2\theta = 2.94^\circ$ (30.0 Å) arises from the smectic layer (d_{001}), and a broad one in the range between 14 and 20° (maximum is ca. 16.5° (5.4 Å)) arises from the lateral distance (d_{100}) of the molecules within the layer. The broad feature for the latter reflection indicates that the molecules have no higher order of the arrangement within the smectic layer. From the thermal and X-ray results, the smectic phase is assigned to the A modification (S_A). It is noteworthy that the broad maximum (16.5° (5.4 Å)) is longer than the values for the usual liquid crystals having aromatic rings (ca. 20° (4.4 Å)). That is, the lateral distance of molecules within the layer is ca. 1 Å longer than that of the usual liquid crystals. The profile for **1b** (at 67 °C ($T_{SA-I}-3$ °C)), Fig. 3(b) shows reflection at $2\theta = 3.08^\circ$ (28.7 Å) and a broad one in the range between 14 and 20° (maximum is ca. 16.3° (5.4 Å)). Interestingly, the layer spacing for **1b** is shorter than that for **1a**, while the molecular length of **1b** would be longer than that of **1a**. The profile for **1c** (at 63 °C ($T_{SA-I}-3$ °C)), Fig. 3(c) shows a reflection at $2\theta = 3.10^\circ$ (28.5 Å) and a broad one in the range between 14 and 20° (maximum is ca. 16.7° (5.3 Å)). The intensity of the former reflection is relatively high compared with that of the latter one. Interestingly, the layer spacing for **1c** is the shortest of the three. These facts indicate that the layer spacing of the S_A phase becomes shorter with increasing the carbon number of the hydrocarbon chain.

As shown in Fig. 3, the relative intensity of the reflection for d_{001} to d_{100} is apparently dependent on the hydrocarbon chain length. The intensity ratio for the even member (**1b**) is fairly high. On the other hand, the ratios for the odd members (**1a** and **1c**) are very low. These results may also be concerned with the even-odd effect of the hydrocarbon

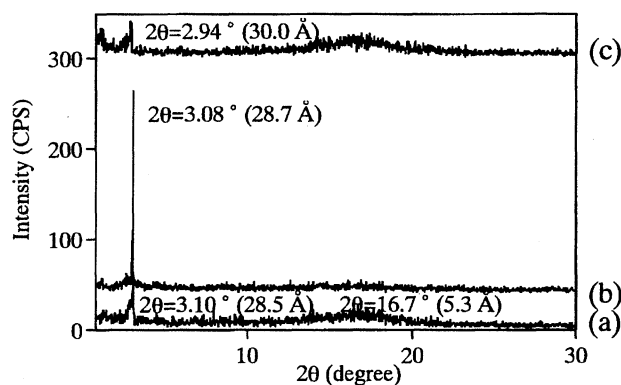


Fig. 3. X-Ray profiles for **1a**, **1b**, and **1c**. a; **1a** at 75 °C ($T_{SA-I}-9$ °C), b; **1b** at 67 °C ($T_{SA-I}-3$ °C), and c; **1c** at 63 °C ($T_{SA-I}-3$ °C).

chain length.

Molecular Structure and Molecular Arrangement in the S_A Phase: The molecular structures of **1** were estimated by a semi-empirical molecular orbital calculation (AM1 method in MOPAC, Ver. 6.0). In the most stable conformation, the 2-(perfluorooctyl)ethoxyl group extends toward the side plane of the aromatic ring. The longest molecular length for **1a** was calculated to be 22.2 Å. Similarly, the molecular lengths for **1b** and **1c** were estimated to be 23.5 and 24.5 Å, respectively. As can be seen from Fig. 3, the calculated molecular lengths are far shorter than the layer spacings obtained from X-ray analyses. These facts indicate that the molecules form an interdigitated arrangement within the smectic layer. The possible model arrangements for **1b** are illustrated in Fig. 4. In Fig. 4(a) for **1b**, the hydrocarbon moieties involving the aromatic rings are piled up on one another, and the fluoroalkyl chains arrange outside of the layer; also and the entire layer is surrounded by fluoroalkyl chains, where the intermolecular distance is 5.4 Å on the average. In

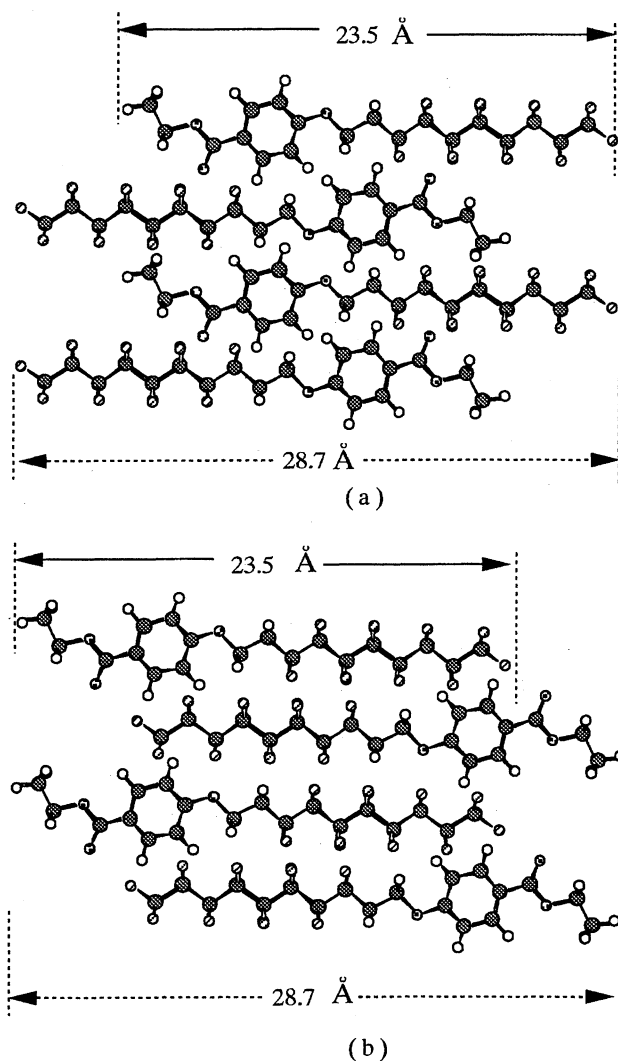


Fig. 4. Possible molecular arrangements for **1b**. The layer spacings were obtained from X-ray analyses. The molecular lengths were estimated by calculation (refer to text).

model (b) in Fig. 4, on the other hand, the fluoroalkyl chains are piled up around the center of the layer, and the entire layer is surrounded by hydrocarbon chains. In both cases, a fluorophilic interaction around the fluoroocetyl chains must play an important role for maintaining the layer structure. In model (a), however, the elongation of the hydrocarbon chain would interact with the fluorophilic interaction and destabilize the layer structure; also, the layer spacing must be independent of the hydrocarbon chain length. In model (b), on the other hand, the elongation of the hydrocarbon chain would be irrespective of the fluorophilic interaction, and the layer spacing would be a function of the hydrocarbon chain length.

In practice, the S_A -I transition temperature decrease with increasing the hydrocarbon chain length, and the layer spacing is almost independent of the hydrocarbon chain length. These results are in good agreement with model (a).

Usually, a lateral substituent is known to reduce the mesomorphic properties, since it increases the molecular breadth, and reduces the geometrical anisotropy. As shown in Table 1, interestingly, the S_A -I transition temperatures for the bromo and nitro compounds, **2** and **3**, are very similar to that of **1**. These results may be concerned with the fact that in these systems the molecular distance within the layer (5.4 Å

on average) is fairly large compared with that of the usual liquid-crystalline materials (ca. 4.5 Å); thus, the lateral substituents are accommodated in the space without changing the lateral distance.

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