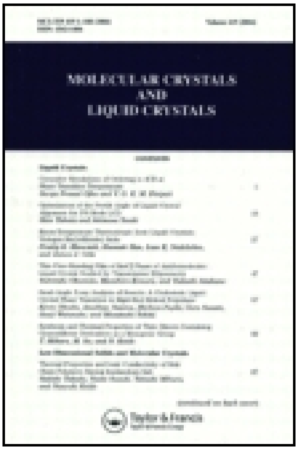

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Synthesis and Thermal Properties for α,ω-Bis{3-Nitro-4-(2-Perfluorooctyl)-Ethoxybenzoyloxy}Alkanes

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Synthesis and Thermal Properties for α,ω-Bis{3-Nitro-4-(2-Perfluorooctyl)-Ethoxybenzoyloxy}Alkanes

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This paper describes thermal properties and molecular arrangements for α, ω-bis{3-nitro-4-(2-perfluorooctyl)ethoxybenzoyloxy}alkanes. The homologous series shows a smectic A (SmA) phase as well as higher ordered smectic one, and the layer structure of the SmA phase is examined by X-ray diffraction. The phase transition behavior and layer structure are notably influenced by the central alkylene chain length. These results are compared with those for the corresponding monomeric liquid crystals.

Keywords: liquid crystal dimer; molecular arrangement; perfluoroalkyl chain; smectic A phase; X-ray diffraction

INTRODUCTION

Liquid crystal (LC) dimers containing two mesogenic units connected with a flexible alkylene chain have been synthesized intensely to study their mesomorphic properties [1,2]. One of the main characteristics of these compounds is the obvious even-odd alternation of the phase behavior accompanied by the carbon number of the central alkylene chain. Furthermore, it is known that the layer structures of smectic phases in LC dimers have the variation in the layer spacing, such as so-called monolayer, intercalated, and interdigitated types.

Previously, we have reported that alkyl 4-(2-perfluoroalkyl)ethoxybenzoates and the related compounds show interesting physico-chemical

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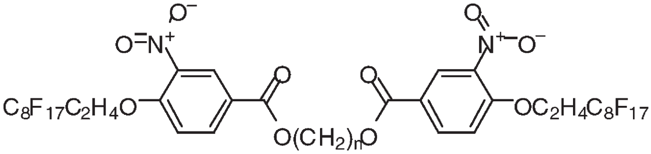
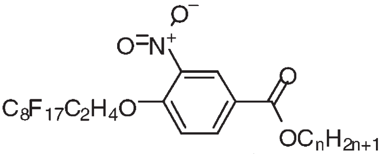


Compounds **1**



Compounds **2**

FIGURE 1 Chemical structures for compounds **1** and **2**.

properties due to a fluorophilic and/or fluorophobic interactions around the perfluoroalkyl groups [3–8].

In this paper, we prepared the following LC dimers **1** and monomeric compounds **2**, and investigated the thermal behavior and the molecular arrangements in smectic A (SmA) phase by means of X-ray diffraction studies.

EXPERIMENTAL

Compounds **1** and **2** were prepared by the method described in our earlier paper [3]. X-ray diffraction experiments for the SmA phases were performed using a Rigaku-denki RINT 2200 diffractometer, where CuKα ($\lambda = 1.541\,\text{Å}$) was used as an X-ray source. The reflection angle was calibrated by a comparison of both right and left angles. The temperature was controlled using a Rigaku PTC-20A controller. The samples filled into the quartz capillaries (1.5 mmϕ) were oriented by a constant magnetic field (480 G). The samples were heated to the isotropic temperature and the measurements were carried out during the cooling process. The molecular lengths were calculated by a semi-empirical molecular orbital calculation, where minimization of the total energy was achieved by an AM1 method [9].

RESULTS AND DISCUSSION

Transition temperatures and latent heats for **1** and **2** are summarized in Table 1. The thermal properties for **2** have been partially reported in our earlier papers [3,4]. All nine members of the series for **1** and

TABLE 1 Transition Temperatures and Latent Heats for **1** and **2**

		Transition temperature (°C)							Latent heat (kJ mol^{-1})		
Compounds	n	C		SmX		SmA		I	mp	SmX–SmA	SmA–I
1	2	•	136	(•	103)	•	161	•	40.3	14.5	3.5
	3	•	158	–		•	163	•	36.5		4.7
	4	•	149	(•	123)	•	165	•	58.8	14.2	5.8
	5	•	118	(•	109)	•	151	•	49.3	15.8	6.0
	6	•	135	(•	117)	•	145	•	59.4	15.7	8.3
	7	•	120	(•	109)	•	137	•	51.3	16.8	7.3
	8	•	131	(•	109	•	130)	•	78.8	*	10.1
	9	•	86	•	104	•	127	•	54.1	15.8	9.7
	10	•	132	–		(•	121)	•	89.2		9.2
2	2	•	95	–		(•	81)	•	41.0		3.3
	3	•	81	–		(•	80)	•	38.9		4.6
	4	•	73	(•	54	•	72)	•	39.2	9.2	4.9
	5	•	75	(•	48	•	74)	•	34.1	7.8	5.9
	6	•	70	–		•	68)	•	31.8		5.3
	7	•	74	(•	58	•	69)	•	29.3	6.3	5.8
	8	•	65	(•	62)	•	66	•	24.8	4.2	3.9
	9	•	71	(•	66	•	70)	•	34.5	5.8	8.5
	10	•	72	(•	70	•	71)	•	31.8	4.8	7.0

C, SmX, SmA, and I indicate crystal, smectic X, smectic A, and isotropic phases, respectively. *; Latent heat for SmX–SmA transition could not be detected due to a recrystallization.

2 exhibit a smectic A (SmA) phase with a focal-conic fan and isotropic textures under homogeneous and homeotropic alignments, respectively. The ethylene, tetramethylene, and later homologues for **1** also show another kind of smectic phase with a broken focal-conic fan texture. This smectic phase has an optically uniaxial nature. The latent heats for the smectic–SmA transition are larger than those for the SmA–I transition, indicating that the smectic phase has a higher order of molecular arrangement. The SmA–I transition temperature for **1** is higher than those for **2** by 50–80°C.

Figure 2 shows transition temperatures for **1** and **2** plotted against the carbon number (n). The SmA–I transition temperature for the lower members (n = 2–4) for **1** gradually increases on ascending the homologues without an even-odd alternation, while those for higher members (n = 4–10) steeply decrease with a weak even-odd alternation as shown in Figure 2(a). The SmX–SmA transition temperatures also show the even-odd alternation except the ethylene homologue.

The SmA–I transition temperatures for **2** gradually decrease with the even-odd alternation on ascending the homologues. The

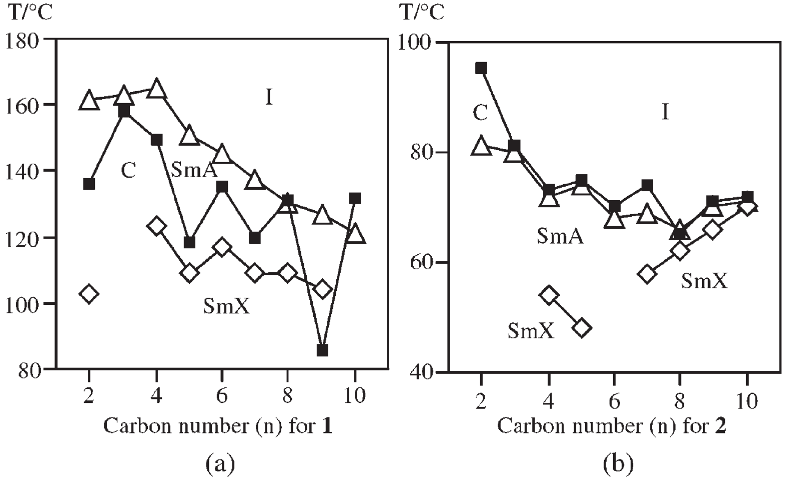


FIGURE 2 Plots of transition temperature vs. carbon number for **1** and **2**. The phase transition below the melting point indicates a monotropic process.

SmX–SmA transition temperature for the lower members decreases on ascending the homologues, while those for the higher members gradually increase. These thermal behaviors for **2** are similar to the results reported previously [3,4].

The phase transition behavior and layer structure of the SmA phase for **1** were further characterized by X-ray diffraction measurements. The X-ray profiles for the SmA phase consist of three reflection peaks: the first peak is a sharp reflection which appears in the range between $2\theta = 2.0$ and 3.0°, the second one is assigned to be the second order of the first one, and the other is a broad one around $2\theta = 20^\circ$. The layer spacing of the SmA phase is calculated from the first peak. Examples of the small angle range are shown in Figure 3.

For the pentamethylene homologue of **1** in Figure 3(a), the intense reflection peak at $2\theta = 2.45^\circ$ (36.0 Å) appears at the SmA temperature range, and the reflection angle gradually shifts to 2.25° (39.2 Å) with decreasing temperature during the SmA phase. Below the SmX–SmA transition temperature, the reflection angles stay constant through the SmX temperature range. A similar trend could be observed in the odd members of **1**.

For the hexamethylene homologue of **1** in Figure 3(b), on the other hand, the intense reflection peak at $2\theta = 2.04^\circ$ (43.3 Å) appears during the SmA temperature range, and the reflection angle stay constant throughout the SmA and SmX temperature ranges.

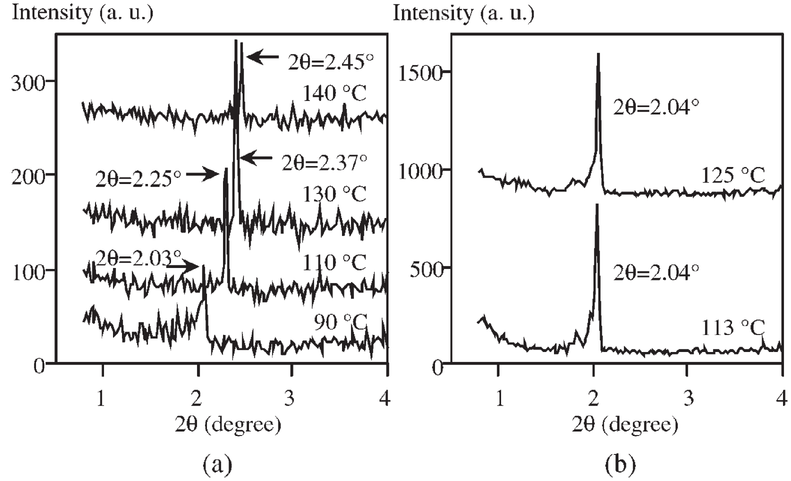


FIGURE 3 X-ray profiles for **1** (a); the pentametylene (n = 5) homologue and (b); the hexamethylene (n = 6) homologue.

The layer spacing calculated from the peak top of the reflection is plotted against temperature in Figure 4. For the odd members of **1** in Figure 4(a), the layer spacing gradually increases with decreasing a temperature during the SmA phase, and shows the notable change

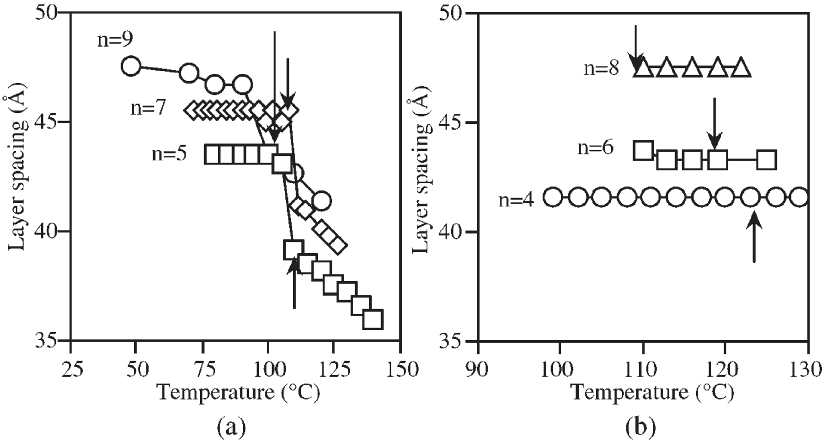


FIGURE 4 Plots of the layer spacing vs. temperature for **1** (a); the odd homologues and (b); the even homologues. n indicate the carbon number of the central alkylene chain. The arrows indicate the SmA–SmX transition temperatures.

around the SmA–SmX transition point. The layer spacing in the SmX phase is almost independent of temperature.

On the other hand, the layer spacing for the even members of **1** stays constant thoughout the SmA and SmX temperature ranges. Interestingly, the layer spacing in the SmA phase resembles that in the SmX phase.

In order to consider the molecular arrangement in the SmA phase, the molecular structure was estimated by a semi-empirical molecular orbital calculation (MOPAC97), where the minimization of the heat of formation was achieved by an AM1 method [9]. The molecular shape and the longitudinal length are mainly determined by the terminal perfluoroalkyl chains, two ester groups, and central alkylene chain, where we supposed that the alkyl and alkylene chains have a zigzag conformation so as to keep the linearity as shown in Figure 5.

In the model, two extreme conformations **L** and **B** are possible with respect to the benzene–COO bond. The molecular orbital calculation suggests that the energy difference between conformers **L** and **B** is 0 kcal mol^{-1} in practice.

For the pentamethylene homologue for **1**, molecular lengths for conformer **L** and **B** are calculated to be 44.6 and 39.2 Å, respectively.

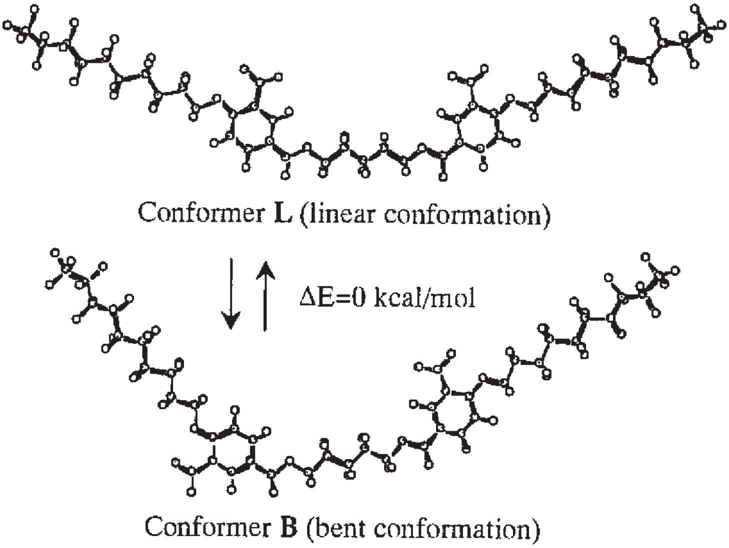


FIGURE 5 Two extreme conformations for the pentamethylene homologue of **1**. ΔE indicates the energy difference in the heat of formation between conformers **L** and **B**, calculated by MOPAC97.

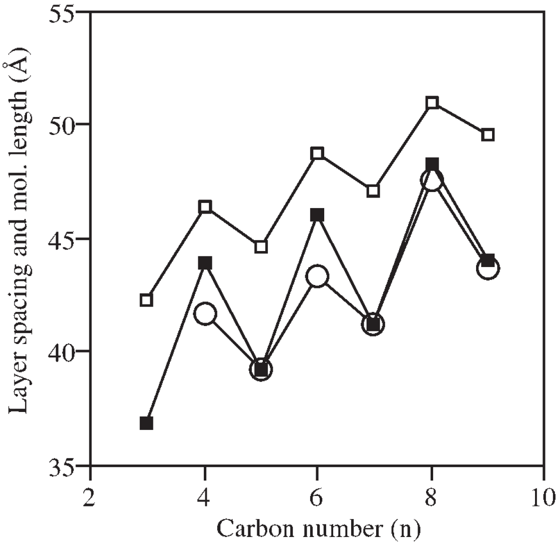


FIGURE 6 Plots of molecular length and layer spacing vs. carbon number (n) for **1**. □, ■, and ○ indicate the molecular length for conformers **L**, **B**, and the layer spacing in the SmA phase near the SmX–SmA transition point.

Similarly, the molecular lengths for the conformers **L** and **B** of the other homologues are calculated, and the results are plotted against the carbon number (n) as shown in Figure 6. In the Figure 6, the layer spacing for the SmA phase near the SmX–SmA transition point is also plotted.

The molecular lengths for conformers **L** and **B**, and the layer spacing show the even-odd alternation, where those for the even homologues are longer than those for the odd ones. Interestingly, in the odd homologues and the octamethylene one, the layer spacing has a good agreement with the molecular length for conformer **B**. For example, the layer spacings in the SmA phase for pentamethylene, heptamethylene, octametylene, and nonamethylene homologues are 39.2 (39.2), 41.2 (41.2), 47.5 (48.2), and 43.7 (44.0) Å, respectively, where the parentheses indicate the molecular lengths for conformer **B**.

As can be seen from Figure 5, conformer **B** has a bent molecular shape and seems to be not suitable for displaying the LC properties in general. According to our assumption that the convenient packing of the bent molecules is responsible for high smectic properties [10], however, conformer **B** is suitable for the formation of the smectic phases. In addition to the molecular shape, the electrostatic nature around the perfluoroalkyl chain, such as fluorophilic and/or fluorophobic effects also assists the formation of the smectic phases.

CONCLUSION

We have synthesized a series of dimeric compounds **1**, which exhibit SmA and highly ordered smectic phases. The even-odd alternation is slightly observed in the SmA–I transition temperatures for higher members, but not for lower members. These results are in contrast to the general observation for other liquid crystal dimers.

The X-ray diffraction studies revealed that the even-odd alternation is observed in the layer spacings of the SmA phase.

Further examination is now underway.

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