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A New Mesomorphism of the Alkyl 4-(2-Perfluoroalkyl)ethoxybenzoate Derivatives

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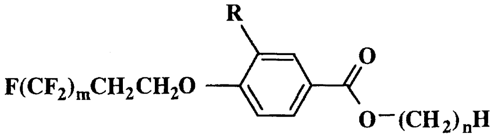
The liquid-crystalline properties of the homologous members of alkyl 4-(2-perfluorooctyl)ethoxy-3-R-benzoates (R = H (**1**), NO_2 (**3**), Br (**4**)) show a new mesomorphic behavior. The lower alkyl (methyl–pentyl) esters of **1** exhibit a smectic A phase, and the smectic A-isotropic transition temperature tends to decrease with increasing the carbon number of the alkyl group, where the layer spacing of the smectic A phase tends to become short with increasing carbon chain length. The hexyl–decyl esters are non-mesogenic, and the after members again show a smectic A phase. The similar trend has been found for **3** and **4**. Homologous members of alkyl 4-(2-perfluorodecyl)ethoxybenzoates (**2**) also show a similar thermal behavior. The smectic properties are strongly dependent on the relative constitution of the perfluoroalkyl group to the alkyl one within the molecule. The molecular arrangement of the smectic A phase is discussed.

A large number of liquid-crystalline materials incorporating a perfluoroalkyl group have been synthesized,[1,2] and some of them are important materials for display devices. It has been known that the perfluoroalkyl group tends to induce smectic properties.[3—9] Probably, a fluorophilic interaction around the perfluoroalkyl group plays an important role for the layer arrangement of molecules. In our earlier paper we described that homologous members of alkyl 4-(2-perfluorooctyl)ethoxybenzoates (**1**) show a new phase behavior.[10] That is, the lower esters (methyl–pentyl) show a smectic A phase, where the smectic A-isotropic transition temperature decreases with increasing the alkyl chain length, and the hexyl and heptyl esters are non-mesogenic, even in the rapid cooling process. This phase behavior is quite rare in the usual liquid-crystal systems, and is a characteristic property of the new system.

This paper describes a further examination of the mesomorphic properties of **1** and the related compounds **2**—**4** (Chart 1).

Experimental

Materials. 2-(Perfluorooctyl)- and 2-(perfluorodecyl)ethanols were purchased from Daikin Kogyo Co. and were used without further purification. The alcohols and 3-nitro- and 3-bromo-4-hydroxybenzoates were reacted using the Mitsunobu reaction,[11] giving corresponding compounds **1**, **2**, **3**, and **4**. The purity of the compounds was checked by NMR spectroscopy and a DSC thermogram using a "DSCPURITY" program (Seiko-denshi Co.).



		m	R
Compounds	**1**	8	H
	2	10	H
	3	8	NO_2
	4	8	Br

Chart 1.

Method. The transition temperatures and latent heats were determined 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 using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). 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 was crammed into a quartz capillary (1.5 mmϕ) and heated to the isotropic temperature, a measurement was carried out on the cooling process.

Results and Discussion

The transition temperatures and latent heats for the homologous members of **1** are summarized in Table 1. Compounds **1a**—**1e** show a monotropic smectic phase with a focal conic fan texture showing an optically uniaxial nature. Interestingly, the smectic–isotropic transition temperature gradually decreases with increasing the carbon number of the alkyl chain. As mentioned in our earlier paper,[10] the smectic phase was assigned to the A modification (S_A). The latent heat also decreases slightly with increasing the carbon number of the alkyl chain. Compounds **1f**—**1j** do not show any mesophase, even during a rapid cooling process. Interestingly, **1k**—**1p** show a monotropic smectic phase with a focal conic fan texture with an optically uniaxial nature similar to that of **1a**—**1e**. However, the S_A–I transition temperatures

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

		Transition temperature[a)]				(T/°C)	Latent heats (kJ mol^{-1})	
Compounds	n	C		S_A		I	ΔH_{C-I}	ΔH_{S_A-I}
1a	1	·	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	
1g	7	·	77	—		·	46.5	
1h	8	·	69	—		·	43.3	
1i	9	·	71	—		·	50.3	
1j	10	·	73	—		·	52.7	
1k	11	·	72	(·	56)	·	52.8	7.4
1l	12	·	61	(·	58)	·	72.0	8.2
1m	13	·	69	(·	61)	·	59.6	8.2
1n	14	·	66	(·	63)	·	81.2	9.0
1o	15	·	67	(·	65)	·	78.7	8.0
1p	16	·	71	(·	66)	·	91.9[b)]	

a) C, S_A, and I indicate crystal, smectic A, and isotropic phases, respectively. Parentheses indicate a monotropic transition temperature. b) Total latent heats for C–I and S_A–I transitions.

for these members gradually increase with increasing the carbon number of the alkyl chain. The transition temperatures are plotted against the carbon number of the alkyl chain in Fig. 1.

The S_A–I transition temperatures for the lower members steeply decrease while displaying an even–odd alternation. The higher members show the S_A phase, and both S_A phases are immiscible in the diagram.

In order to characterize these two S_A phases, binary phase diagrams were examined; the results are shown in Fig. 2.

The smectic–isotropic transition temperatures of the binary mixtures continuously change while displaying a downward concavity, indicating that both smectic phases of **1c** and **1l** are miscible in any composition. A similar trend was observed for a mixture of **1e** and **1k**. From these results, both S_A phases are miscible with each other in the mixed states, while these S_A phases are discontinuous in the pure state (Fig. 1(a)).

A similar trend is observed in the perfluorodecyl derivatives **2**, as shown in Table 2. The homologous members of **2** exhibit higher S_A–I transition temperatures than those of **1** in ca. 20 °C. The enhancement of the S_A–I transition temperature should concern an extension of the rigid perfluoroalkyl group and an increase in the fluorophilic interaction around the perfluoroalkyl groups. Compound **2c** shows two kinds of smectic phases, where the smectic phases of the higher and lower temperature regions show the optical properties. As shown in Table 2, a smectic-smectic transition accompanies a large latent heat. Considering the fact that many compounds having a long perfluoroalkyl chain show a smectic B phase,[9)] the smectic phases at the low-temperature region could be assigned to the S_B phase.

Compounds **3** and **4** also show the S_A phase when the alkyl group is short. Similar to **1**, the S_A–I transition temperatures of these systems decrease while displaying an even–odd alternation, with increasing the carbon number of the alkyl chain, as shown in Figs. 2(c) and 2(d). Interestingly, the S_A–I transition temperatures are close to those of the corresponding members of **1**, while **3** and **4** have a large lateral substituent. The lower smectic phase for **3d** and **3e** is miscible with the S_B phase of **2c**.

The S_A phase was further characterized by X-ray diffraction measurements. The X-ray profile for **1a** shows a sharp reflection at $2\theta = 2.94°$ (30.0 Å) arising from the smectic layer (d_{001}), and a broad one between 14 and 20° (maximum is ca. 16.5° (5.4Å)) arising from the lateral distance (d_{100}) of the molecules within the layer. Here, the angles are an average, because the samples were not oriented against the X-ray beam. The broad feature for the latter reflection indicates that the molecules have no higher order of molecular arrangement within the smectic layer. From the thermal and X-ray results, the smectic phase has been confirmed to be the A modification. It is noteworthy that the broad maximum is longer than the values for the usual liquid crystals having aromatic rings (ca. 20° (4.4 Å)). That is, the lateral distance of the molecules within the smectic layer of new compounds is ca. in 1 Å longer than that of the usual liquid crystals.[12)] The members, **1k**—**1p**, show the S_A phase with focal conic fan textures similar to those of the earlier members. However, the X-ray experiment was achieved with only one member (**1l**), because of recrystallization.

The X-ray data and molecular lengths of new compounds are summarized in Table 3.

The molecular lengths were estimated by semi-empirical molecular orbital calculations (MOPAC, Ver. 6.0), where the most stable conformation was determined by the AM1 method. The layer spacings for **1a**—**1d** decrease with increasing the carbon number of the alkyl chain, while the calculated molecular lengths increase. The ratios of the layer spacing to the molecular length are always larger than one,

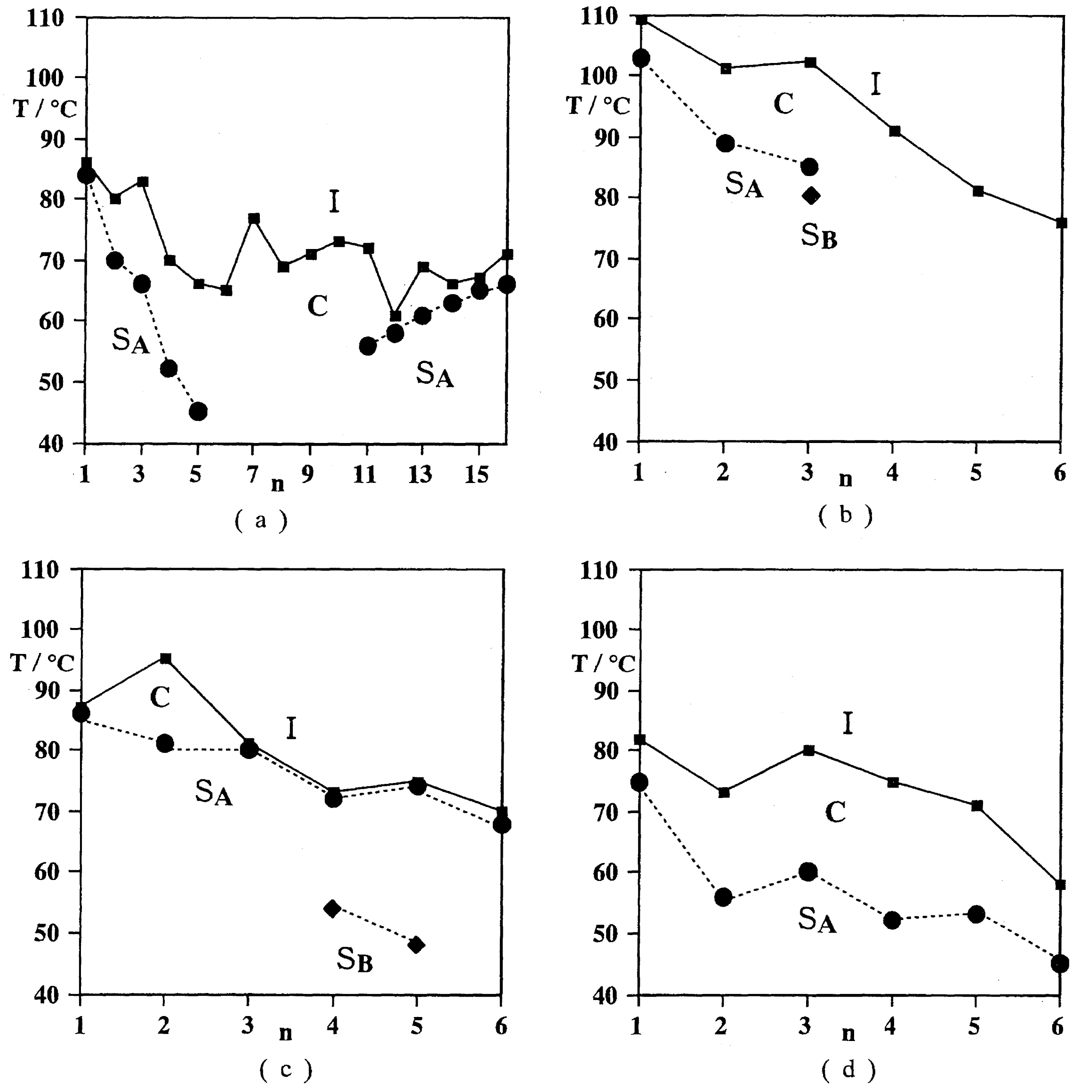


Fig. 1. Plots of transition temperatures for (a); **1**, (b); **2**, (c); **3**, and (d); **4**. Dashed lines indicate a monotropic transition.

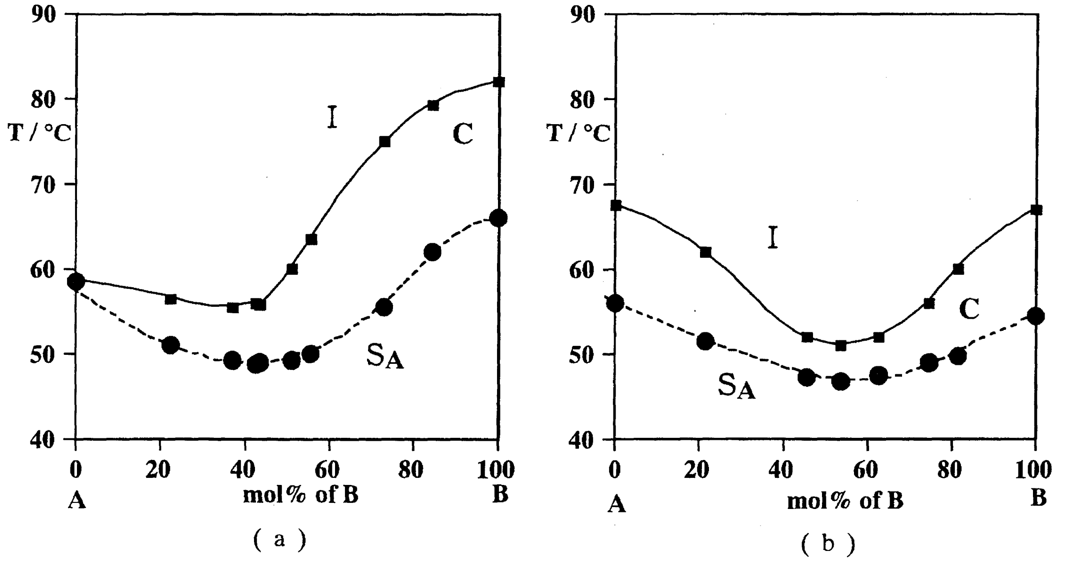


Fig. 2. Phase diagrams for the mixtures of (a); **1c** (A) and **1l** (B), and (b); **1e** (A) and **1k** (B). Dashed lines indicate a monotropic transition.

Table 2. Transition Temperatures and Latent Heats for **2**—**4**

		Transition temperatures				(T/°C)			Latent heats (kJ mol^{-1})		
Compounds	n	C		S$_B$		S$_A$		I	$\Delta H_{C\text{–}I}$	$\Delta H_{S_B\text{–}S_A}$	$\Delta H_{S_A\text{–}I}$
2a	1	·	109	—		(·	103)	·	51.5		6.6
2b	2	·	101	—		(·	89)	·	56.3		5.5
2c	3	·	102	(·	78	·	85)	·	50.0	12.3	5.1
2d	4	·	91	—		—		·	47.1		
2e	5	·	81	—		—		·	53.6		
2f	6	·	76	—		—		·	56.6		
3a	1	·	87	—		(·	86)	·	32.3		2.4
3b	2	·	95	—		(·	81)	·	41.0		3.3
3c	3	·	81	—		(·	80)	·	38.9		4.6
3d	4	·	73	(·	54	·	72)	·	39.2	9.2	4.9
3e	5	·	75	(·	48	·	74)	·	34.1	7.8	5.9
3f	6	·	70	—		(·	68)	·	31.8		5.3
4a	1	·	82	—		(·	75)	·	43.1		3.4
4b	2	·	73	—		(·	56)	·	35.1		2.6
4c	3	·	80	—		(·	60)	·	39.4[a]		
4d	4	·	75	—		(·	52)	·	39.9[a]		
4e	5	·	71	—		(·	53)	·	38.5[a]		
4f	6	·	58	—		(·	45)	·	30.6[a]		

a) Total latent heats for C–I and S$_A$–I transitions.

Table 3. X-Ray Diffraction Data and Molecular Lengths

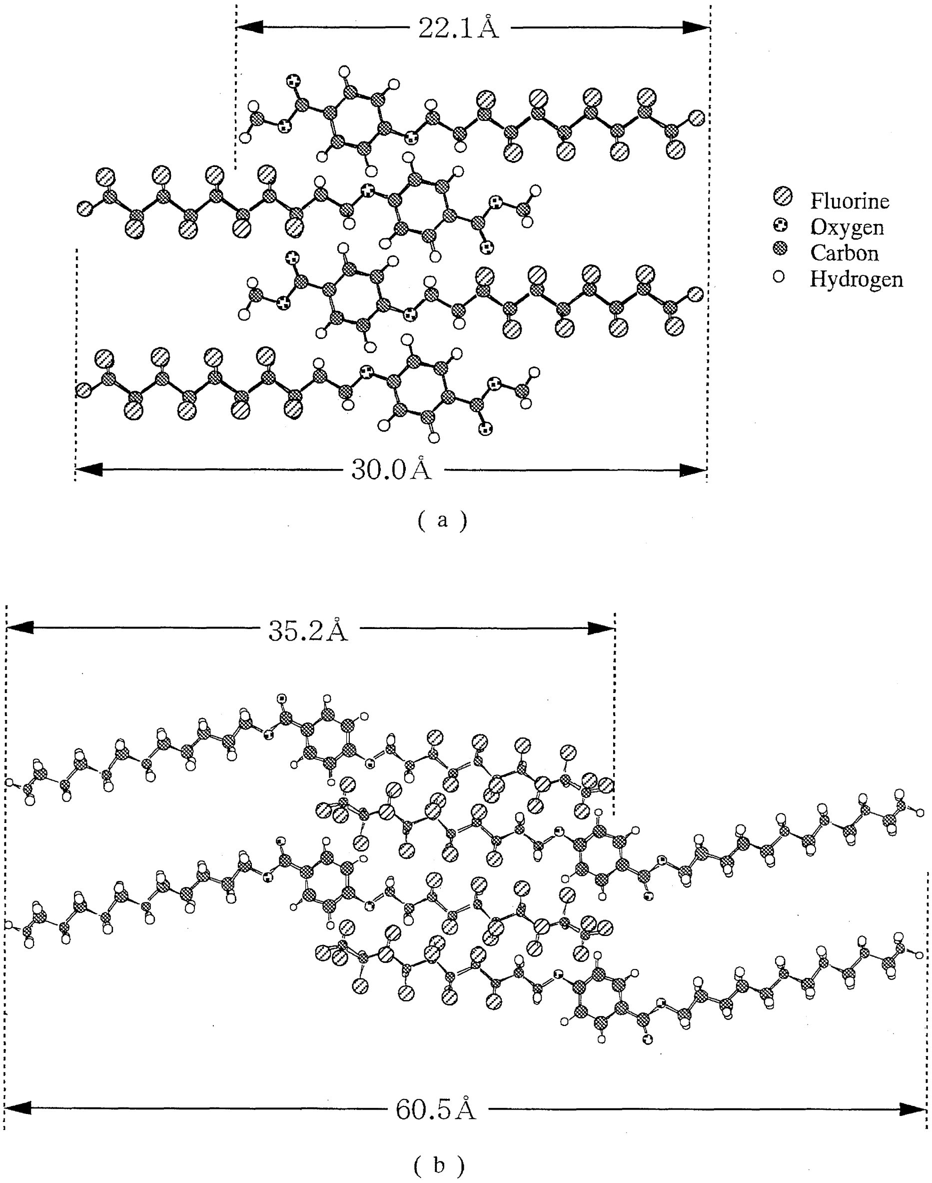
Compound	Temp	2θ	Layer spacing	Calcd molecular	d/l
	°C	deg.	d/Å	length l[a]/Å	
1a	78	2.94	30.0	22.1	1.36
1b	67	3.08	28.7	23.5	1.22
1c	63	3.10	28.5	24.5	1.12
1d	35	3.16	27.9	25.8	1.08
1l	56	1.46	60.5	35.2	1.72
2a	90	2.42	36.5	24.5	1.49
2b	82	2.60	34.0	25.8	1.32

a) Molecular lengths for the most stable conformer were calculated by an AM1 method (MOPAC ver. 6.0).

indicating that the molecular packing in the S$_A$ phase is not a simple monolayer arrangement. An interesting fact is that the ratio of the layer spacing to the molecular length becomes small with increasing the carbon number of the alkyl chain. On the other hand, the layer spacing for **1l** is far larger than the calculated molecular length, where the ratio of the layer spacing to the molecular length is 1.72. A similar trend is also recognized in **2**. However, their ratios of the layer spacing to the calculated molecular length are larger than those of the corresponding members of **1**. The layer spacings for **2a** and **2b** are ca. 6 Å longer than those of **1a** and **1b**. A noteworthy fact is that the value is close to twice that of the tetrafluoroethylene unit.

These results indicate that the fluororphilic interaction is very important in maintaining the layer structure of the molecules. Two models of the molecular arrangement are shown in Fig. 3. As can be seen from Fig. 3(a), the interaction between the perfluoroalkyl groups is supposed to be of primary importance for maintaining the layer structure of the molecules, since the alkyl group does not increase the layer spacing, as shown in Table 3. In this model, the inter-molecular distance is on average 5.4 Å, and is longer than the breadth (ca. 4.5 Å) of the benzene ring of the usual liquid-crystalline materials.[12)] The extension of the molecular distance would be concerned with the long and rigid perfluoroalkyl group. In this model, the short alkyl group is accommodated in the perfluoroalkyl groups, and the long alkyl group interrupts a fluorophilic interaction, thus decreasing the thermal stability of the layer structure without changing the layer spacing. This model also agrees with the fact that the layer spacing for **2a** and **2b** is ca. in 6 Å longer than that of **1a** and **1b**, where 6 Å is close to twice that of the tetrafluoroethylene unit. On the other hand, Fig. 3(b) shows a model layer structure for **1l** with a separate arrangement of perfluoroalkyl and alkyl groups. As shown in Fig. 1(a), the layer arrangement of the molecules is facilitated not only by the fluorophilic interaction around the perfluoroalkyl groups, but also by the hydrophilic interaction around the long alkyl groups. Both smectic layers have no affinity in the homologous members, as shown in Fig. 1(a), but are miscible with each other in mixed states, as shown in Figs. 2(a) and 2(b).

Conclusively, the fluorophilic interaction around the perfluoroalkyl groups is of primary importance in maintaining the smectic structure, and the thermal stability of presented compounds is strongly dependent on the relative constitution of the perfluoroalkyl group to the alkyl one within their molecules.



(a)

(b)

Fig. 3. Possible molecular arrangements in smectic A phases for (a); **1a** and (b); **1l**. The molecular lengths for the most stable conformations were obtained by an AM1 method (MOPAC ver. 6.0).

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