

Liquid crystalline properties of some compounds having a perfluoroalkyl group

Hiroaki Okamoto *, Naonobu Yamada, Shunsuke Takenaka

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan

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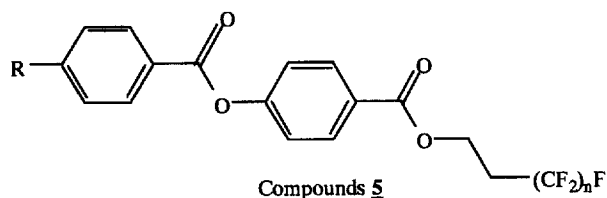
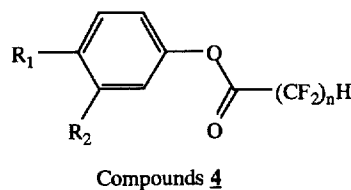
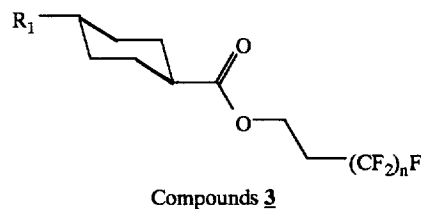
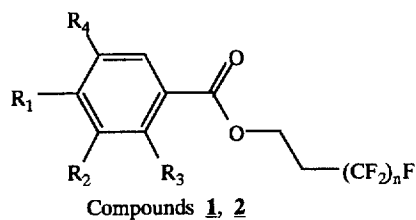
Abstract

The paper describes the liquid crystalline properties of 2-(*n*-perfluoroalkyl)ethyl *para*-, *meta*-, and/or *ortho*-substituted benzoates, and some related compounds. Most of the *ortho* and/or *meta*-substituted derivatives show a smectic B phase, while the *para*-substituted ones are non-mesogenic. When the substituent is a nitro or a cyano group, many derivatives show a smectic A, as well as a B phase. The corresponding 4-*trans*-alkylcyclohexanecarboxylates are non-mesogenic. *Meta*- or *para*-substituted phenyl ω -hydroperfluoroalkanoates are also non-mesogenic. From these results, we conclude that in order to show liquid crystalline properties for the present systems, the substituents at *meta* and/or *ortho* positions, orientation of the ester group, and the rigid perfluoroalkyl group are very important. X-ray study indicated that the smectic A and B phases for polar liquid crystals have a partially bilayer and bilayer arrangements, respectively. The smectic B phase for non-polar liquid crystals have a monolayer arrangement. Thermal motion around the perfluoroalkyl group is assumed to be almost frozen in both phases. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Liquid crystals; Smectic properties; Substituent effect; Perfluoroalkyl group

1. Introduction

Generally, the core of liquid crystals consists of a two or three-ring systems in order to hold the anisotropy of the molecular structure. In practice, however, a large molecular shape is not desirable in point of application since it increases the viscosity, melting point, and so on. We assume that many researchers have tried to prepare liquid crystals having a single-benzene ring as a core. However, single benzene ring compounds may not so readily show liquid crystalline properties because of insufficient geometrical anisotropy, except for a few examples such as *para*-alkyl- or alkoxybenzoic acids [1], and benzene hexa-alkanoates [2].



* Corresponding author.

In previous papers, we described that a perfluoroalkyl group tends to enhance the thermal stability of liquid crystalline phases, especially, smectic A and C phases, due to rigidity of the perfluoroalkyl moiety [3–5]. In this paper, we describe the substituent effect on the mesomorphic properties of 2-perfluoroethyl benzoates and some related compounds.

2. Experimental

2.1. Method

IR spectra were measured by a Horiba FT-200 infrared spectrometer. ^1H and ^{13}C NMR spectra were measured on a Nihon-Denshi EX-270 spectrometer in chloroform-*d* solution, and ^{13}C –CP/MAS spectra were measured on a Nihon-Denshi CMX-300 spectrometer. X-ray diffraction was measured with a Rigaku RINT 1500 X-ray diffractometer. Transition temperatures and latent heats were determined by using a Seiko SSC-5200 differential scanning calorimeter (DSC), where Indium (99.9%) was used as a calibration standard (m.p., 156.6°C, $\Delta H = 28.4$ J/g). The DSC thermogram was operated at a heating or a cooling rate of 5°C/min. Phase transitions were observed by using a Nikon X2-PT 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 crammed into a quartz capillary (1.5 mm ϕ) was heated to the isotropic temperature, a measurement was carried out on the cooling process.

2.2. Preparation

The esterification of the acids and the phenols was carried out according to the previously reported method [6], where a vigorous stirring of the reaction mixture is indispensable when the perfluoroalkanol is long. 1,1,2,2-Tetrahydro-perfluorodecyl 2-nitrobenzoate (**1s**): To a solution of 2-nitrobenzoyl chloride (4.0 g, 24 mmol) and 1,1,2,2-tetrahydro-perfluorodecanol (8.9 g, 19 mmol) in dry toluene (30 ml), dry pyridine (30 ml) was added dropwise with vigorous stirring at 50°C, and the solution was heated at 80°C for 4 h. The resulting solution was dried in vacuo, and the residue was purified by column chromatography on silica gel using chloroform as eluent, followed by sublimation in vacuo, giving a colorless oil; yield 10.6 g (89%) The purity was checked by a DSC thermogram by using a 'DSCPURITY' program (Seiko-Dennshi) instead of elementary analysis, giving 99.8% purity. IR (KBr disc): 1740 (ν_{COO}), 1538, 1352 (ν_{NO_2}). ^1H NMR (CDCl_3): δ 7.97–7.94 (1H, m), 7.75–7.63 (3H, m), 4.65 (2H, t, $J = 6.6$ Hz), 2.69–2.51 (2H, m) ppm. ^{13}C NMR (CDCl_3): δ 165.1, 148.1, 133.1, 132.0, 129.8, 127.1, 124.1, 58.1 ($J_{\text{C-F}} = 4.8$ Hz), and 30.2 ($J_{\text{C-F}} = 22.0$

Hz) ppm. The other materials were prepared by a similar method.

3. Results

3.1. Thermal properties

Table 1 shows the thermal properties of mono-substituted benzoate esters.

1a–1g and **1m–1n** having a long perfluoroalkyl group and a substituent at the *para* position show high melting points, and any mesophase was not observed. In order to estimate the mesomorphic properties of the *para*-substituted derivatives, the binary phase diagram for the mixture of **1o** and **1c** was examined, and the results are shown in Fig. 1.

In Fig. 1a, both compounds form an eutectic mixture at 39°C. Both smectic–isotropic (S–I) and smectic–smectic (S–S) transitions were reduced by increasing molar concentration of **1c**, and hidden by the solid phase at around 30 mol% of **1c**. These results indicate that the *para*-substituted derivatives have intrinsically poor mesomorphic properties.

On the other hand, some *meta*- and *ortho*-substituted derivatives show one and/or two kinds of mesophases having a focal conic fan texture and a broken one. A typical example is shown in Fig. 2. **1o** shows two kinds of mesophases; the upper mesophase has a typical focal conic texture and tends to form a homeotropic texture between glass surfaces (Fig. 2a). The lower mesophase shows a broken fan texture (Fig. 2b). The textures of these phases are easily broken by slipping the glass cover. These textures are optically uniaxial. The Upper and lower smectic phases were assigned to be the $A(S_A)$ and $B(S_B)$ modifications, respectively, considering the results of the X-ray diffraction experiments, as shown in the later part. **1h** and **1i** having a polar substituent at the *meta* position, show a stable mesophase having a focal conic texture. As shown in Fig. 1b, the mesophase of **1h** is miscible with the S_B phase of **1o**. The methyl and fluoro derivatives (**1j** and **1l**) also form a monotropic S_B phase. On the other hand, the methoxy derivative (**1k**) is non-mesogenic, probably due to the large volume.

The melting and clearing points rapidly decrease with decreasing carbon number of the fluorocarbon chain.

The nitro and cyano derivatives (**1o** and **1p**) show two monotropic smectic phases. The upper smectic phase is miscible with the smectic A phase of **5c** in Table 2, where the S_A –I transition shows a linear correlation with the molar composition. On the other hand, the methyl and fluoro derivatives (**1q** and **1r**) show only an S phase, where the transition temperatures are low. Some *ortho*-substituted derivatives also show a smectic phase with a focal conic texture, though the clearing points are lower than those for the *meta*-substituted ones. The nitro derivative (**1s**) shows S_A and S_B phases, while methyl and methoxy derivatives (**1u**, and **1v**) show only an S phase.

Table 1
Transition temperatures of compounds 1

Compounds	R_1	R_2	R_3	n	C	S_B	S_A	I
1a	CH ₃	H	H	10	•	63	—	•
1b	CH ₃ O	H	H	10	•	66	—	•
1c	C ₂ H ₅ O	H	H	10	•	65	—	•
1d	C ₁₀ H ₂₁ O	H	H	10	•	77	—	•
1e	F	H	H	10	•	74	—	•
1f	CN	H	H	10	•	118	—	•
1g	CF ₃	H	H	10	•	60	—	•
1h	H	NO ₂	H	10	•	62	• 92	•
1i	H	CN	H	10	•	77	• 90	•
1j	H	CH ₃	H	10	•	60	(• 54)	•
1k	H	CH ₃ O	H	10	•	63	—	•
1l	H	F	H	10	•	63	(• 60)	•
1m	CN	H	H	8	•	93	—	•
1n	C ₄ H ₉	H	H	8	•	32	—	u ^a
1o	H	NO ₂	H	8	•	65	(• 44	• 53)
1p	H	CN	H	8	•	70	(• 41	• 48)
1q ^{ac}	H	CH ₃	H	8	•	55	(• -7)	•
1r ^a	H	F	H	8	•	27	(• 7)	•
1s	H	H	NO ₂	8	•	26	• 26	• 39
1t	H	H	Cl	8	•	17	—	•
1u ^a	H	H	CH ₃	8	•	28	(• 77)	•
1v ^a	H	H	CH ₃ O	8	•	12	(• -5)	•
1w ^a	H	NO ₂	H	6	•	44	—	(• 2)
1x ^{ac}	H	CN	H	6	•	19	—	(• -6)
1y	H	H	Cl	6	•	2	—	•

^a The smectic phase has not been characterized.

From these results, we conclude that in the present system, a substituent at the *meta* or the *ortho* position plays some important roles for displaying the mesomorphic properties, and a polar group such as a cyano or a nitro group at the lateral position tends to facilitate the formation of the S_A phase.

Table 3 shows thermal properties of some di-substituted benzoate derivatives. **2** have a long alkoxy group at the *para* position of the aromatic ring, and substituent(s) at the lateral position. **2a** having a nitro group at the *meta* position shows S_B and S_A phases, which were confirmed by the miscibility diagram. **2c** having a bromine at the *meta* position forms only an S_B phase. As we can see from Fig. 1c, the S_A - I transition steeply decreases with increase in concentration of **2c**, and the S_B - S_A (I) transition shows a maximum at 80 mol% of **2c**. The diagram suggests that **2b** and **2c** are poor in showing S_A properties.

A similar trend was also observed in **2h** and **2j**. From these results, we assume that in order to display liquid crystalline phases for *para*-alkyl or alkoxy derivatives, the *meta* substituent is preferable. However, two lateral substituents are not suitable for liquid crystallinity (**2e** and **2i**). **2d**, **2f**, and **2g** having a substituent at the *ortho* position are non-mesogenic. Probably, the *ortho* substituent brings about the conformational change around the ester group due to a steric hindrance.

For the comparative study, we prepared some cyclohexanecarboxylate derivatives of **1**, and the transition temperatures of 1,1,2,2-tetrahydro-perfluoroalkanoyl *trans*-4-pentyl-

cyclohexanecarboxylates (**3**) are summarized in Table 4. **3a** and **3b** have similar melting points to the corresponding aromatic derivatives such as **1n**, and do not show any mesophase even on cooling process. In order to estimate the liquid crystal properties, the binary phase diagram for the mixture of **3a** and **1o** was examined, as shown in Fig. 1d. As is evident from the figure, **3a** is poor in liquid crystalline properties.

For the comparative study, we prepared some *meta*- or *para*-substituted phenyl ω -hydroperfluorononanoates (**4**), and the transition temperatures are summarized in Table 5.

The derivatives were very unstable, and were very easily hydrolyzed by moisture. It is assumed that a rotation around the ether bond of the ester linkage of **4** is easier than in **1**, and decreases the rigidity and linearity of the entire structure. As we can see from the table, all derivatives are non-mesogenic, and the melting points are also low.

Table 2 shows the transition temperatures of 1,1,2,2-tetrahydroperfluoro-alkanoyl 4-(4-substituted phenyl)benzoates (**5**).

For the homologous series the smectic morphism is dependent on both terminal alkoxy and perfluoroalkyl chain lengths. That is, elongation of the alkoxy group induces a smectic C phase, while that of the perfluoroalkyl group enhances the transition temperatures.

3.2. X-ray diffraction study of the smectic phases

As mentioned above, the smectic phases for the single benzene system have an optically uniaxial nature, and the

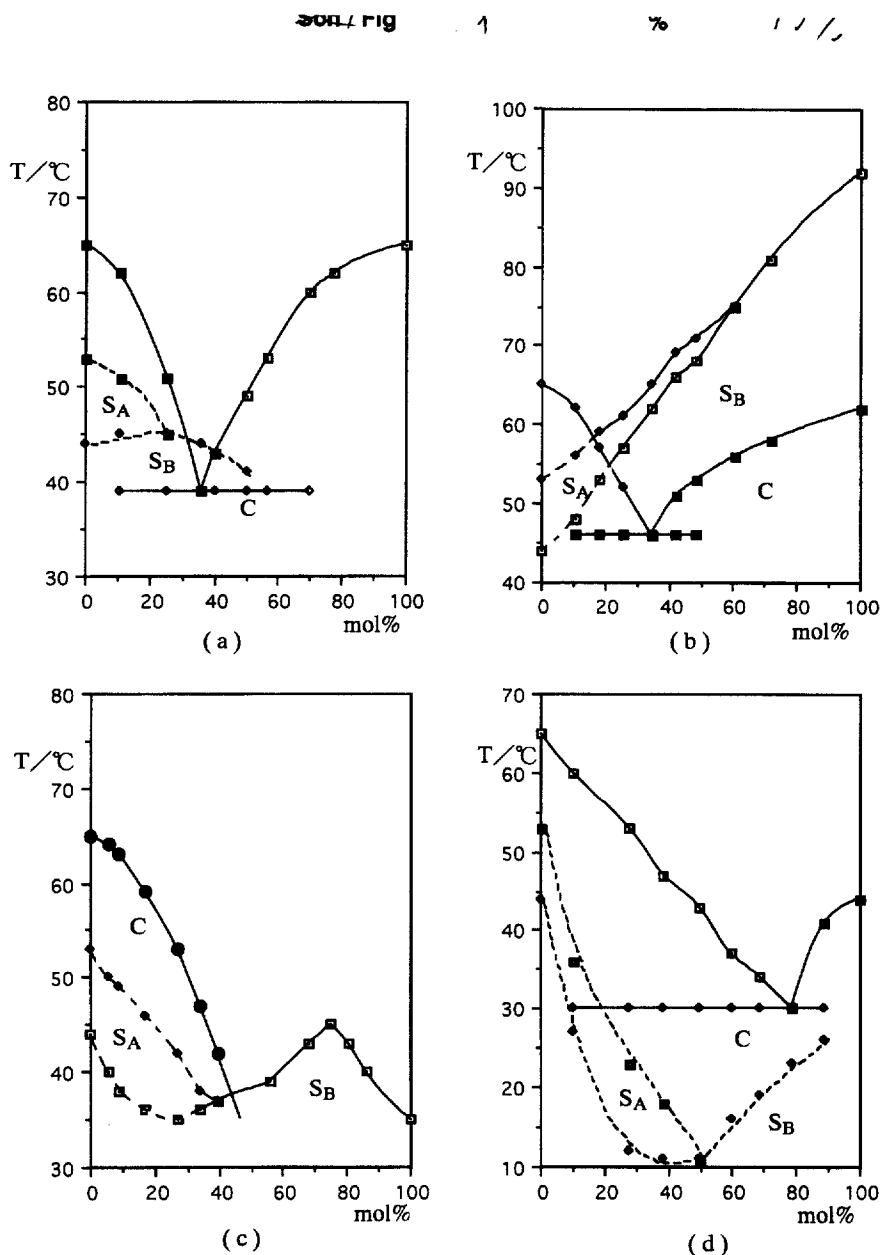


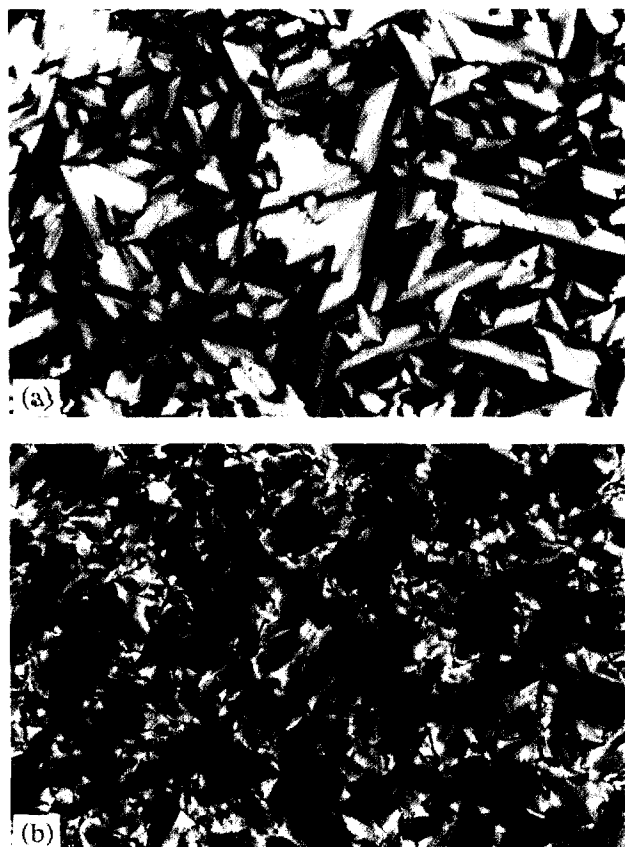
Fig. 1. Phase diagrams for the mixtures of: (a) **1o** and **1c**, (b) **1o** and **1h**, (c) **1o** and **2c**, and (d) **1o** and **3a** on left and right, respectively. C, S_A , and S_B indicate crystal, smectic A and B phases, respectively. Dashed lines indicate a monotropic transition.

textures of smectic phases show a typical focal conic or the broken texture.

The X-ray diffraction patterns of both smectic phases for **1s** and **2c** are shown in Figs. 3 and 4, respectively. The profile at 28°C shows reflection maxima at $2\theta = 2.56^\circ$ (34.5 Å), 5.18° (17.0 Å), and 7.86° (11.2 Å) as well as a broad maximum around 16° (ca. 5 Å). The upper smectic phase is assigned to the S_A modification with a layer spacing of 34.5 Å. The profile at 20°C (Fig. 3b) corresponding the S_B phase shows intense peaks at $2\theta = 2.18^\circ$ (40.5 Å), 6.66° (13.3 Å), and 13.4° (6.6 Å), and so on. The complex feature indicates that this phase has a high translational order. Considering the fact that the texture of this phase has an orthogonal nature, this smectic phase is assumed to be a B modification.

The molecular structure of **1s** was calculated by the MM2 method, and the structure and possible molecular arrangements in the smectic phases are shown in Fig. 5.

The calculated molecular length of **1s** is 19 Å, where the perfluoroalkyl and fluoromethylene groups account for 13 and 11 Å, respectively. The molecular arrangement model in Fig. 5a satisfies the layer spacing of the S_A phase (34.5 Å). The appearance of the peak at 7.86° (11.2 Å) suggests that in the smectic A phase, the fluoromethylene chain is rigid, and keeps the zig-zag conformation. On the other hand, the layer spacing of the smectic B phase changes to 40.5 Å which agrees with twice the molecular length, indicating that the molecules form a bilayer arrangement, as shown in Fig. 5a. Interestingly, a peak at 6.66° corresponding to the perfluoro-

Fig. 2. Micrographs for **10**: (a) S_A phase at 50°C, and (b) S_B phase at 41°C.Table 2
Transition temperatures of compounds **5**

Compounds	R_1	n	C	S_C	S_A	I
5a	C_4H_9O	4	•	94	—	• 133 •
5b	C_4H_9O	6	•	104	—	• 151 •
5c	C_4H_9O	8	•	117	—	• 168 •
5d	$C_8H_{17}O$	4	•	71	• 109	• 111 •
5e	$C_8H_{17}O$	6	•	88	• 122	• 129 •
5f	$C_8H_{17}O$	8	•	101	• 131	• 145 •

Table 3
Transition temperatures of compounds **2**

Compounds	R_1	R_2	R_3	R_4	n	C	S_B	S_A	I
2a	$C_6H_{13}O$	NO_2	H	H	8	• 44	•	• 49	• 51 •
2b ^a	$C_6H_{13}O$	Br	H	H	8	•	•	• 30	—
2c ^a	$C_8H_{17}O$	Br	H	H	8	•	•	• 35	—
2d	$C_6H_{13}O$	H	CH_3	H	8	• 14	—	—	•
2e	$C_6H_{13}O$	Br	H	Br	8	• 52	—	—	•
2f	$C_6H_{13}O$	H	CH_3	H	6	• 15	—	—	•
2g ^b	$C_6H_{13}O$	H	Cl	H	6	• 2	—	—	•
2h	$C_6H_{13}O$	Br	H	H	6	• 3	(• -8)	—	•
2i ^b	$C_8H_{17}O$	Br	H	Br	6	• 51	—	—	•
2j ^b	$C_8H_{17}O$	Br	H	H	6	• 19	(• -7)	—	•

^a The crystalline phase was not obtained.^b The smectic phase has not been characterized.Table 4
Transition temperatures of compounds **3**

Compounds	R_1	n	C	I
3a	C_5H_{11}	8	•	• 44 •
3b	C_5H_{11}	6	•	• 10 •

Table 5
Transition temperatures of compounds **4**

Compounds	R_1	R_2	n	C	I
4a	$C_8H_{17}O$	H	8	•	• 45 •
4b	H	H	8	•	• 45 •
4c	H	CH_3	8	•	• 9 •
4d	H	NO_2	8	•	• 27 •

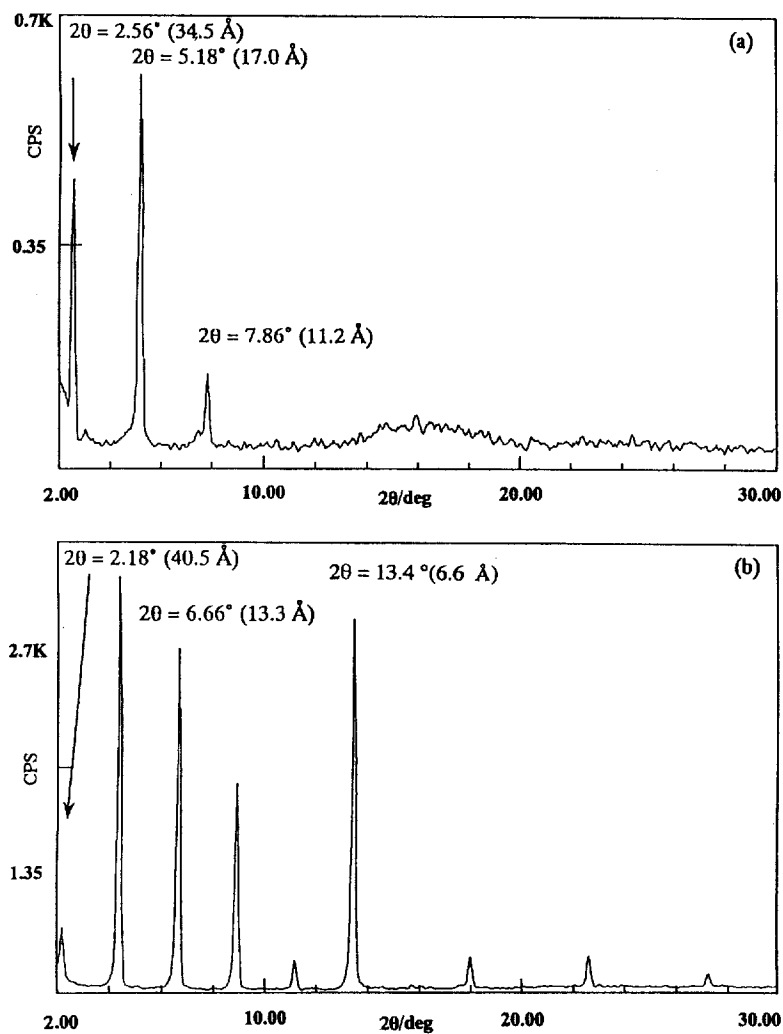
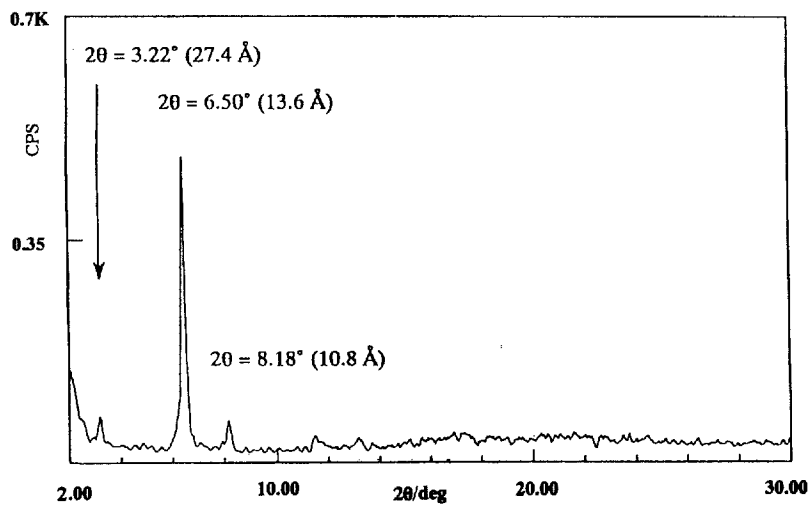
roalkyl chain length (13 Å) becomes more intense than the peak at 7.86°. This indicates that the rigidity of the perfluoroalkyl chain plays a very important role for the formation of the smectic B phase.

Fig. 4 shows the X-ray profile for the smectic B phase of **2c**. The calculated molecular length of **2c** (Fig. 5b) is 27 Å, where the perfluoroalkyl group accounts for 13.5 Å. As shown in Fig. 4, the diffraction peak corresponding to the molecular length is observed at 3.22°. In addition, the profile shows an intense peak at 6.50° (13.6 Å) corresponding to the perfluoroalkyl chain length. These facts indicate that the perfluoroalkyl groups have high translational order in the smectic phase, and the rotation is almost frozen.

Further analysis of the X-ray profiles is now underway.

3.3. NMR studies

The ^{13}C NMR spectra of **1s** in liquid crystalline and solid phases are shown in Fig. 6. The assignment of the ^{13}C NMR spectrum of **1s** in $CDCl_3$ solution is also indicated in Fig. 6. The carbons of the perfluoroalkyl chain are observed in the

Fig. 3. X-ray profiles for 1s (a) S_A phase at 28°C (b) S_B phase at 20°C.Fig. 4. X-ray profiles for 2c S_B phase at 20°C.

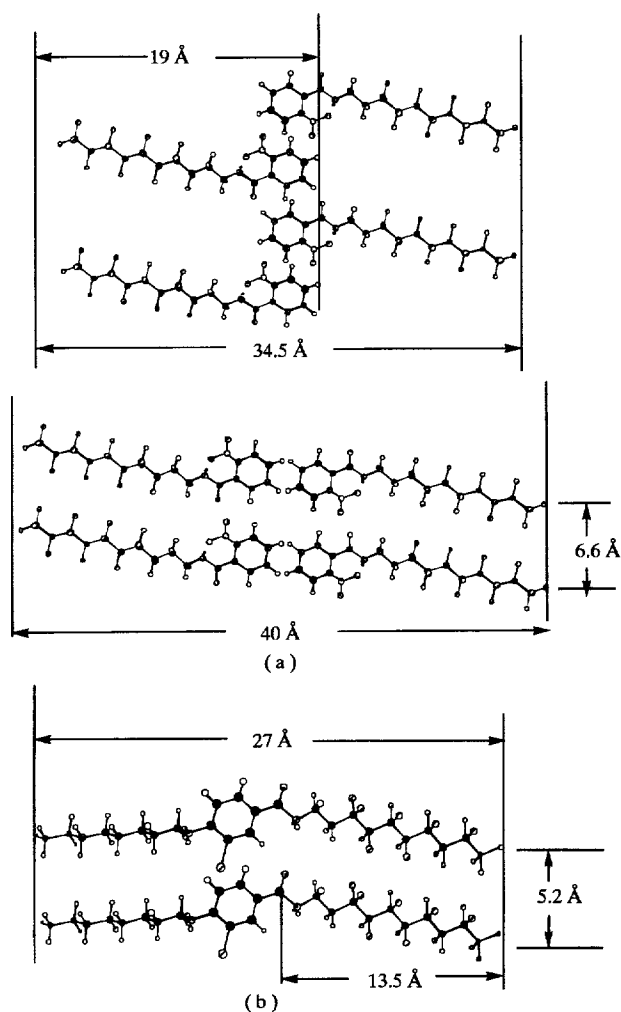


Fig. 5. Possible molecular arrangement models for (a) S_A (upper) and S_B (lower) phases of **1s** and (b) S_B phase of **2c**.

range 100 and 120 ppm as broad peaks due to coupling with fluorine atoms. Fig. 6a shows the MAS/DD spectrum (at 2.0 kHz) for the S_A phase (at 30°C). The spectrum in the S_A phase is similar to those in solution, and the chemical shifts are in agreement with those of the solution spectrum within 0.2 ppm.

Fig. 6b shows the MAS/DD spectrum (at 2.0 kHz) in the S_B phase (at 18°C). The spectrum and chemical shifts of the peaks are similar to those in the S_A phase, although each peak is broad. It has been considered that molecules in both S_A and S_B phases have a layer structure and keep a rotational freedom with the longitudinal axes of the molecules orthogonal to the layer. A difference is that the molecules in the S_B phase have hexagonal packing, while those in the S_A phase are random [7].

On the other hand, the profile of the CP/MAS spectrum (Fig. 6c) in the solid phase (at 0°C) is different from the former. All peaks become sharp, and the singlet peak at 165

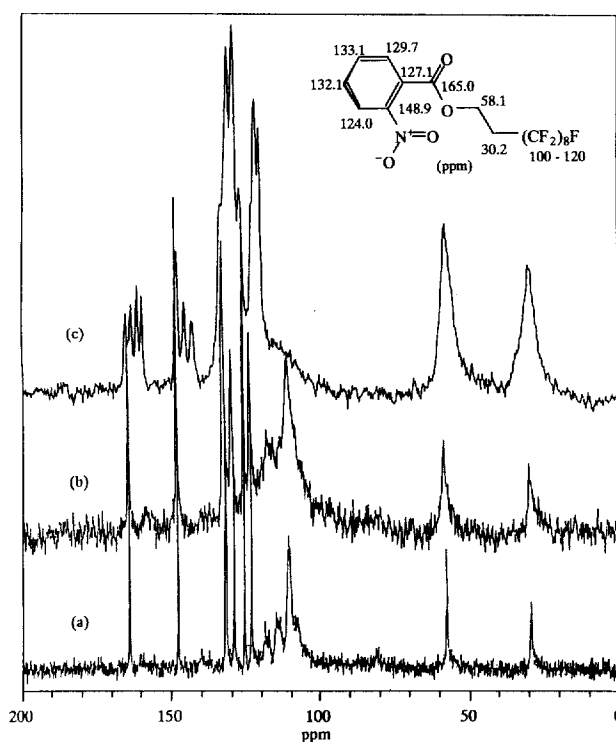


Fig. 6. ^{13}C NMR spectra of **1s**: (a) S_A phase at 30°C (MAS/DD, 2.0 kHz, 75.5 MHz) (b) S_B phase at 18°C (MAS/DD, 2.0 kHz, 75.5 MHz) (c) solid phase at 0°C (CP/MAS, 6.2 kHz, 75.5 MHz). The values in the structure indicate ^{13}C NMR chemical shifts for **1s** in CDCl_3 (10 W/W%) at 25°C (proton decoupled, 67.8 MHz).

ppm arising from the ester carbon splits to four peaks at 166.7, 162.9, 161.2 ppm in addition to the original. Similarly, the singlet peak at 149.5 ppm arising from the carbon (C–NO₂) splits to three peaks at 149.5, 147.1, and 144.4 ppm. The spectrum indicates that the rotation of the aromatic ring is restricted in the solid phase, and some conformers that are exposed in different circumstances are present.

3.4. Conclusion

In perfluoroalkyl substituted benzoate systems, perfluoroalkyl group and some *ortho* and *meta* substituents play important roles in enhancing the smectic A and B phases, and polar substituents such as cyano and nitro groups facilitate the formation of the smectic A phase.

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