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Synthesis and Thermal Properties of Some Benzenes Incorporating a Perfluoroalkyl Chain

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Some homologs of ortho-, meta-, and/or para-substituted phenyl 1*H*, 1*H*, 2*H*, 2*H*-perfluorodecyl ethers have been synthesized. The most of para-substituted phenyl ethers show a smectic phase, while the para-long alkyloxycarbonylated derivatives are non-mesogenic. The ortho- or meta-substituted derivatives show a low liquid crystalline phase with a low clearing point. On the other hands, for the corresponding 1*H*, 1*H*, 2*H*, 2*H*-perfluoroalkyl benzoate systems, para-substituted benzoate derivatives are non-mesogenic and the lateral substituted ones are mesogenic. From these results, we conclude that in order to show liquid crystalline properties, the roles of the substituents and the perfluoroalkyl chain differ with the ether homologs and the ester homologs. For both systems, however, the rigidity and the linearity of the perfluoroalkyl group are a primary importance for displaying the liquid crystalline properties.

Introduction

Generally, a lateral substituent is known to be unfavorable for mesomorphic properties, since it decreases not only the geometrical anisotropy but also the polarizable anisotropy of molecules.^{1, 2)} On the other hands, in the homologs of 1*H*, 1*H*, 2*H*, 2*H*-perfluoroalkyl benzoates, the lateral substituents are indispensable for mesomorphic properties.^{3, 4)} The roles of the lateral substituent have not been clarified.

In this paper, we describe the thermal properties of homologs of 1*H*, 1*H*, 2*H*, 2*H*-perfluoroalkoxy-benzenes (compounds 1), compared with homologs of 1*H*, 1*H*, 2*H*, 2*H*-perfluoroalkyl benzoates (compounds 2), and taking note of the substituent and perfluoroalkyl chain effects.

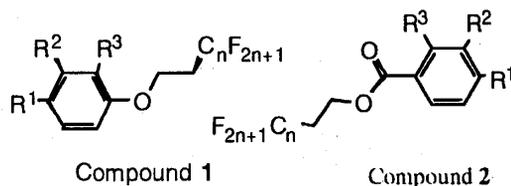


Fig. 1

Experimental

IR spectra were taken as KBr discs using Horiba FT-200 infrared spectrometer. ¹H and ¹³C NMR spectra were measured by Nihon-Denshi EX-270 spectrometer in chloroform-d solution, chemical shifts were expressed in the unit δ. The solid state ¹³C NMR (CPMAS) measurement was made with a Chemagnetics JNM-CMX300 spectrometer operating at 300.2 and 75.6 MHz for ¹H and ¹³C, respectively. Transition temperatures and latent heats were determined by using Seiko SSC-5200 differential scanning calorimeter (DSC), where Indium (99.9%) was used as a calibration standard (mp., 156.6 °C, ΔH=28.4 J/g). The DSC thermogram was operated by a heating rate or a cooling one 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. Phase types were identified on the basis of their microscope texture only.

Preparation of Methyl 3-nitro-4-hydroxy-benzoate.

Into a 300 ml round-bottomed flask 20 ml of concentrated nitric acid was cooled by means of an ice bath to 0-10 °C, and then, with stirring, there is added gradually a 10.0 g (65.7 mmol) of methyl 4-hydroxy-

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benzoate. During the addition of the benzoate, which required about two hours, the temperature of the reaction mixture should be kept within the range 5-15 °C. After the benzoate had been added, stirring is continued for twenty min. longer: the mixture was then poured into 300 ml of chilled water. The crude product separates as a solid and was filtered off by means of suction and washed with water. The product is recrystallized from ethanol. (A colorless needles; 10.4 g, 52.7 mmol, 80.2%) mp. 72 °C,

IR ν =1540.8 (NO₂), 1718.3 (C=O), and 3226.3 (O-H) cm⁻¹.

Preparation of 4-Methyl 3-nitro-4-(1H, 1H, 2H, 2H-perfluorooctyloxybenzoate (1b).

Into a 50 ml of three necked round-bottomed flask 2-(perfluorooctyl)ethanol (1.0 g, 2.2 mmol), phenol (0.52 g, 2.6 mmol) synthesized above procedure and triphenyl-phosphine (0.69 g, 2.6 mmol) diethyl azodicarboxylate (0.42 ml, 2.64 mmol) was added under atmosphere at room temperature.

After stirring for 8 h, the solvent was evaporated *in vacuo*. The mixture was purified by column chromatography and recrystallized from methanol and ethyl acetate. A colorless needles (0.26 g, 0.45 mmol, 20.6%) IR ν =1542.8 (NO₂) and 1712.5 (C=O) cm⁻¹. ¹H NMR δ =2.77 (2H, tt, *J*=18.1, 6.8 Hz), 3.94 (3H, s), 4.48 (2H, t, *J*=6.8 Hz), 7.16 (1H, d, *J*=8.7 Hz), 8.23 (1H, dd, *J*=8.7, 2.2 Hz), and 8.49 (1H, d, *J*=2.2 Hz) ppm. ¹³C NMR δ =31.1 (*J*_{C-F}=21.9 Hz), 52.5 (*J*_{C-F}=4.9 Hz), 62.1, 113.8, 123.5, 127.2, 135.2, 136.7, 139.7, 154.3, and 164.7 ppm.

Preparation of 4-nitro-1H, 1H, 2H, 2H-perfluorooctyloxybenzene (1f).

A typical procedure was as follows. To a stirred anhydrous THF (20 ml) solution of 4-nitro-phenol (0.46 g, 3.3 mmol), triphenylphosphine (0.86 g, 3.3 mmol), and 2-(perfluorooctyl)ethanol (1.0 g, 2.2 mmol) diethyl azodicarboxylate (0.52 ml, 3.3 mmol) was added under N₂ atmosphere at room temperature. After stirring for 8 h, the solvent was evaporated under reduced conditions. The residue was purified using silica-gel chromatography, and recrystallized from methanol to give 0.26 g (20.6%) of 1f. IR ν =1510.0 and 1342.2 (NO₂) cm⁻¹. ¹H NMR δ =2.69 (2H, tt, *J*=18.1, 6.6 Hz), 4.37 (2H, t, *J*=6.6 Hz), 6.98 (2H, *J*=9.2 Hz), and 8.23 (2H, d, *J*=9.2 Hz) ppm.

Results and Discussion

Table 1 shows the transition temperature for the substituted 1H, 1H, 2H, 2H-perfluorooctyloxybenzenes (compounds 1).

Para-alkoxycarbonyl compounds 1a-1d give considerably high melting points, and any mesophase could not be detected even in rapid cooling, except for the methoxycarbonyl substituted compound 1a and the

nitro substituted compound 1b.

Table 1 Thermal properties of compounds 1

	R ¹	R ²	R ³	n	T / °C	
					C	I
1a	CH ₃ OCO	H	H	8	82 (87)	·
1b	CH ₃ OCO	H	NO ₂	8	84	· 89 ·
1c	CH ₃ OCO	H	Br	8	76	- ·
1d	C ₈ H ₁₇ OCO	H	H	8	69	- ·
1e	CN	H	H	8	46	· 81 ·
1f	NO ₂	H	H	8	41	· 78 ·
1g	H	NO ₂	H	8	55 (41)	·

All the polar substituted compounds 1b and 1e-1g show a smectic phase. The lateral substituted compound 1g shows a smectic phase, monotropically. These results indicate that the lateral substituent is unfavorable for displaying the mesophases.

For compound 1b, the mesophase has a typical focal conic texture and tends to form homeotropic texture between glass surface, where the texture is optically uniaxial. From these results, we conclude that the mesophase is a smectic phase, however, modification of smectic phases is not yet clarified. Interestingly, these smectic phases have a considerably low viscosity, similar to compounds 2.

On the other hands, for comparative studies, the thermal properties of the mono-substituted benzoates 2a-2q and the di-substituted ones 2r-2v are summarized in Table 2.

The perfluoroalkyl benzoates 2 have higher melting point than the corresponding phenyl ethers. In the mono-substituted benzoate systems, all of the para-substituted derivatives 2a-2f, 2j and 2k do not have any mesomorphic properties even in the rapid cooling process, though the meta- or ortho-substituted derivatives have at least one smectic phase. In addition, the polar group such as a cyano group or a nitro one at the lateral position tends to increase the liquid crystallinity. A similar trend is also observed in the di-substituted benzoates 2r-2w. These results indicate that the polar substituent at the lateral position is indispensable for displaying the mesomorphic properties in the benzoate system.

These results indicate that the perfluoroalkyl ester moiety (compounds 2) may be rather rigid than the corresponding ether moiety (compounds 1). Therefore, it is too tight in linearity to display mesophases for compounds 2, and then, the lateral substituent reduces the melting point and displaying

the mesophases. On the other hands, for compounds **1**, it seems that the perfluoroalkyl ether moiety has some flexibility. Therefore, compounds **1** having the long alkyl ester and/or the substituent at the lateral position could not show any mesomorphic properties.

Table 2 Thermal properties of compounds **2**

	R ¹	R ²	R ³	n	C	Transition Temp. (°C)		
						S _B	S _A	I
2a	CH ₃ O	H	H	10	· 66	-	-	·
2b	C ₂ H ₅ O	H	H	10	· 65	-	-	·
2c	C ₁₀ H ₂₁ O	H	H	10	· 77	-	-	·
2d	F	H	H	10	· 74	-	-	·
2e	CN	H	H	10	· 118	-	-	·
2f	CF ₃	H	H	10	· 60	-	-	·
2g	H	NO ₂	H	10	· 62	· 92	-	·
2h	H	CN	H	10	· 77	· 90	-	·
2i	H	CH ₃	H	10	· 60	(· 54)	-	·
2j	CN	H	H	8	· 93	-	-	·
2k	C ₄ H ₉	H	H	8	· 32	-	-	·
2l	H	NO ₂	H	8	· 65	(· 44	· 53)	·
2m	H	CN	H	8	· 19	· 41	· 48	·
2n	H	H	NO ₂	8	· 26	· 26	· 39	·
2o ¹⁾	H	H	CH ₃	8	· 29	(· 17)	-	·
2p	H	NO ₂	H	6	· 44	-	(· 2)	·
2q	H	CN	H	6	· 19	-	(· -6)	·
2r	C ₆ H ₁₃ O	NO ₂	H	8	· 44	· 49	· 51	·
2s ²⁾	C ₆ H ₁₃ O	Br	H	8	·	· 30	-	·
2t	C ₆ H ₁₃ O	CH ₃	H	8	· 14	-	-	·
2u ²⁾	C ₈ H ₁₇ O	Br	H	8	·	· 35	-	·
2v	C ₆ H ₁₃ O	Br	H	6	· 3	(· -8)	-	·
2w	C ₈ H ₁₇ O	Br	H	6	· 19	(· -7)	-	·

¹⁾ The DSC thermogram showed an endotherm at -18 °C.

²⁾ The crystalline phase was not observed.

The flexibility of perfluoroalkyl chain was estimated by using the solid state NMR spectrum. ¹³C NMR spectrum of **1b** in chloroform-d was assigned as shown in Fig. 2, and the CPMAS spectrum in solid phase is shown in Fig. 3.

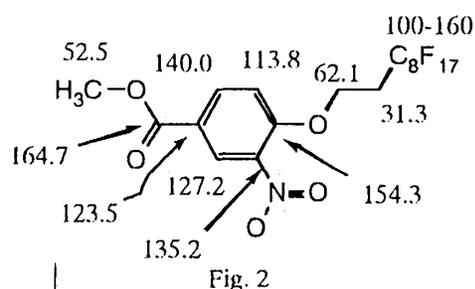
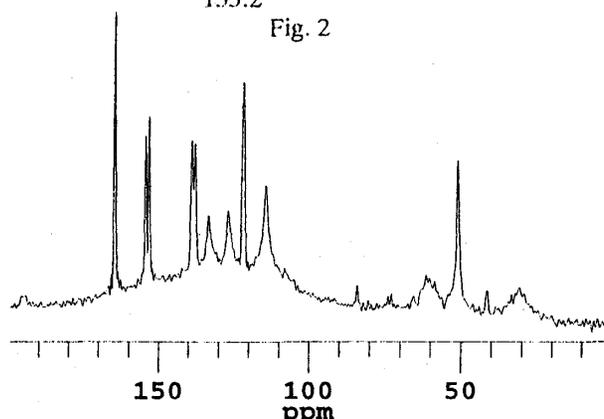


Fig. 2

Fig. 3 ¹³C NMR (CPMAS) spectrum of **1b**

In the solid state, the carbons at the perfluoroalkyl chain are not observed in the range among $\delta=100$ and 160 as broad peaks due to coupling with fluorine atoms. The single peak at $\delta=154.3$ arising from the root carbon of alkoxy group splits to two peaks at $\delta=153.6$ and 154.8. Similarly, the single peak at $\delta=140.0$ splits to two peaks at $\delta=138.3$ and 139.4. These facts indicate that some molecules are exposed in different circumstances, which are similar to perfluoroalkyl benzoate systems (compound **2**)⁴⁾. However, the ethylene carbons (ca. $\delta=30$ and 50) in compound **1b** are observed fairly weak, compared with the perfluoroalkyl benzoates⁴⁾. This result indicates that the perfluoroalkyl ether is more flexible than the perfluoroalkyl ester in the solid state.

Conclusion

The 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyloxybenzenes disclosed a unique thermal property with a low viscosity. It will be worthy of further investigating this smectic properties since these compounds are one of the most simplified materials.

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