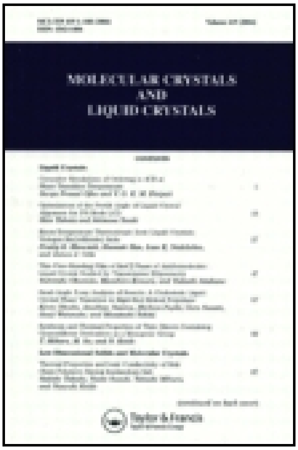

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The Effect of Trifluoromethyl and Difluoromethoxy Groups on Mesomorphic Properties

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The Effect of Trifluoromethyl and Difluoromethoxy Groups on Mesomorphic Properties

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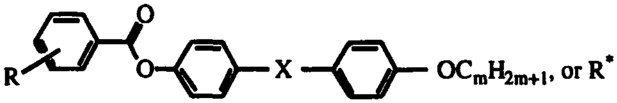
This paper describes the effect of terminal substituent on the mesomorphic properties in 3- and 4-(4-alkoxyphenoxycarbonyl)phenyl 3- and 4-R-benzoate and 4-(4-alkoxybenzoyloxy)phenyl 2-, 3-, and 4-R-benzoates (R = CF_3, OCF_3, OCF_2H). The meta-trifluoromethoxy and para-difluoromethoxy compounds tend to show a smectic C phase, as well as smectic A and nematic ones, and introduction of a chiral carbon in the alkoxyl group induces the chiral smectic C one.

Keywords: liquid crystals; thermal property; Sm C; chiral Sm C; substituent effect; fluorophilic effect

INTRODUCTION

Trifuoromethyl group is one of the important terminal of liquid crystal molecules, and has been known to enhance

smectic properties.[1,2] For the phenomena, we have proposed a new smectic model, where the trifluoromethyl groups arrange around the surface of the smectic layer, and organize a fluorophilic surface.[1] In such conditons, the fluorophilic inter-layer interaction stabilizes the layer structure. In order to further prove the model, we were synthesized some new liquid crystalline materials having fluoromethyl groups, and the thermal properties were examined. In this paper we want to describe the liquid crystalline properties of **1** and **2**, and the results are discussed in terms of the specific interaction around the fluoromethyl group. In addition, chiral liquid crystals having these terminals have been synthesized.



Compounds **1** X = -COO-
Compounds **2** X = -OOC-

EXPERIMENTALS

Preparation of materials and methods were described in our earlier paper.[1]

RESULTS AND DISCUSSION

The transition temperatures for **1** and **2** are summarized in TABLE 1. The members of **1** having a trifluoromethyl group at the para (p) position have been reported to have notable smectic A properties (Sm A).[1]
The members of **2** show a similar phase behavior to **1**. **2a** and **2b** show Sm A and N phases, and the after members

TABLE 1 Transition temperatures of **1** and **2**

Compounds			Transition temperatures(T/°C)								
	R	m	C		Sm C		Sm A		N		I
1a	p-CF_3	8	•	128	-		•	210	-		•
1b	p-OCF_3	8	•	193	-		•	225	-		•
2a	p-CF_3	4	•	206	-		(•	204)	•	220	•
2b		5	•	193	-		•	210	•	214	•
2c		6	•	190	-		•	214	-		•
2d		7	•	190	-		•	213	-		•
2e		8	•	190	-		•	212	-		•
2f	p-OCF_3	8	•	150	-		•	205	•	210	•
2g	p-OCF_2H	8	•	142	•	163	-		•	210	•
2h	m-CF_3	6	•	107	(•	84	•	96	•	101)	•
2i		7	•	110	(•	89	•	98	•	99)	•
2j		8	•	98	(•	88)	•	100	-		•
2k	o-CF_3	7	•	77	-		-		(•	70)	•
2l		8	•	83	-		-		(•	70)	•

Parentheses indicate a monotropic transition.

show only Sm A phase. Interestingly, the Sm A (N)-I transition temperatures are almost independent of m, while these are high enough. The layer spacings for the Sm A phase of **2d**, **2e** and **2f** are 29.7, 30.8, and 32.2 Å, where the molecular lengths (l) calculated by an AM1 method (MOPAC, ver.6.0) are 28.4, 29.6, and 30.9 Å, respectively. We have reported that the layer spacings for the Sm A phase of **1a** and **1b** are 32.1 (l=30.9) and 31.6 Å (l=29.6 Å), respectively.[1] These results indicate that **1** and **2** having a p-trifluoromethyl group form a partially bilayer arrangement in the Sm A phase, and the arrangement is irrespective of the relative orientation of the ester group at the X position.

The meta (m)-trifluoromethyl derivatives, **2h**-**2j**, also exhibit the Sm A phase, though the clearing points are low more than 100 °C compared with those of **2c**-**2e**. The effect of the terminal trifluoromethyl group also seems to be notable, since the ratios of the N-I to Sm A-N transition temperatures are fairly high.[3] Interestingly, these derivatives show a smectic C (Sm C) phase, as well as the Sm A one. These facts suggest that the m-trifluoromethyl group facilitates the tilt arrangement of the molecules within the layer structure.

The o-trifluoromethyl derivatives, **2k** and **2l**, show only an N phase, and the Sm A phase was not exhibited even in rapid cooling process of the N phase. These facts suggest that the o-trifluoromethyl group is poor in induction of smectic phases.

As is evident from the comparison with **2f** and **2g**, interestingly, the terminal trifluoromethoxy group also facilitates the orthogonal arrangement of the molecules within the smectic layer, whilst the difluoromethoxy one does the tilt one. As reported in our earlier paper,[4] the core of **2g**, phenyl 4-(benzoyloxy)benzoate, intrinsically exhibits the Sm C phase. Therefore, we can not refer to the effect of the difluoromethoxy group on the formation of the Sm C phase.

In order to visualize the layer structure of the smectic A phase, and the role of the terminal trifluoromethyl group on the layer formation, the model structure for the Sm A phase of **2e** is shown in Figure 1.

As mentioned above, the layer spacing of 30.8 Å is 1.2 Å longer than the calculated molecular length. In the model, the trifluoromethyl groups arrange around the surface of the

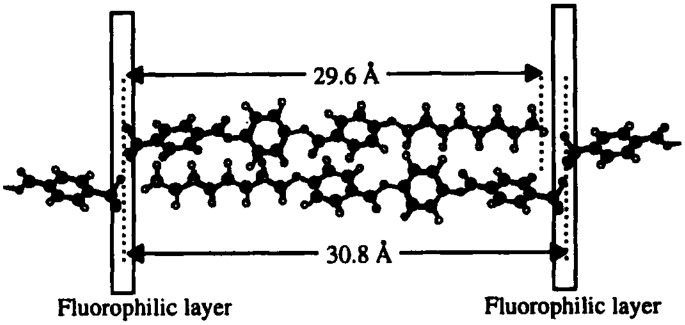


FIGURE 1. Possible molecular arrangement for the Sm A phase of **2e**.

Sm A layer. Therefore, we assume that the fluorophilic interaction around the layer surface effectively stabilizes the layer structure. In the smectic layer of **2g**, however, the fluorophilic interaction would be less than that for **2a**-**2e**, due to substitution of fluorine atoms by a hydrogen. For the m-trifluoromethyl derivatives, **2h**-**2j**, the situation is different a little, since the trifluoromethyl group locates at the meta position of the molecules. As we can assume from Figure 1, the molecules must tilt in order to build up the similar fluorophilic surface. Such fluorophilic surface is impossible to build up in the o-trifluoromethyl derivative, **2k** and **2l**.

Based on these results, we tried to prepare some chiral liquid crystals, as shown in TABLE 2. For **1c** and **1d**, the introduction of the chiral group increases the cholesteric range, but chiral Sm C was not exhibited. In contrast to **1d**, the chiral group in **2m** notably reduces the Sm A thermal stability, and causes of the disappearance of the Sm A phase. Only **2n** exhibited the chiral Sm C phase, where the Ch-I transition temperature was reduced by 80 °C. The m-

TABLE 2 Transition temperatures of chiral liquid crystals

Compounds			Transition temperatures(T/°C)				
	R	R*	C	Sm C*	Sm A	Ch	I
1c	p-OCF_2H	R_1	• 108	-	• 175	• 187	•
1d	p-OCF_2H	R_2	• 98	-	• 189	• 197	•
2m	p-OCF_2H	R_2	• 152	-	-	• 200	•
2n	p-OCF_2H	R_3	• 128	(• 114)	-	• 132	•
2o	m-CF_3	R_3	• 94	-	-	-	•
2p	m-CF_3	R_4	• 154	-	-	-	•

R_1=(S)-$CH_2CH(CH_3)C_2H_5$, R_2=(S)-$(CH_2)_3CH(CH_3)C_2H_5$, R_3=(R)-$CH(CH_3)C_6H_{13}$, R_4=(S)-$CH(CH_3)C_2H_5$. Ch indicates a cholesteric phase. Parentheses indicate a monotropic transition.

trifluoromethyl derivatives, **2o** and **2p** were non-mesogenic. These results indicate that in the present systems the introduction of a branch methyl group at the hydrocarbon chain results in the reduction of not only Sm A and Sm C thermal stability, but also the N one. The examination of the dielectric properties for **2n** is now underway.

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