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## Liquid Crystals

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# Liquid crystalline properties of asymmetric molecules:†

## II. Smectic properties of 4-alkoxyphenyl 4-(4-trifluoromethylbenzoyloxy)benzoates

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The thermal properties of a homologous series of 4-alkoxy-phenyl 4-(4-trifluoromethylbenzoyloxy)-benzoates were examined. The homologues show remarkable smectic properties involving a smectic A and a higher order smectic phase characterized by microscopic and X-ray experiments, indicating that the molecules have a partially bilayer arrangement in both smectic phases. Based on these results, molecular arrangements of the two smectic phases are proposed. The effects of the trifluoromethyl group on the thermal properties of the smectic and crystalline phases are discussed in terms of the fluorophilic interaction around the boundary of the smectic layer.

### 1. Introduction

The trifluoromethyl group is of interest as a terminal or lateral substituent of liquid crystalline molecules [1, 2]: the trifluoromethyl group leads to a dipole moment of 2.84 D for trifluoromethylbenzene, larger than the 0.36 D for toluene. Changes in the nematic-isotropic transition temperatures for some liquid crystalline materials have been correlated with increased dipole moment [3, 4]. Recently, trifluoromethyl compounds have been of interest in connection with their remarkable smectic properties [5]. In chiral liquid crystals the trifluoromethyl group in the side chain may cause the formation of a broad smectic phase with an antiferroelectric nature [6].

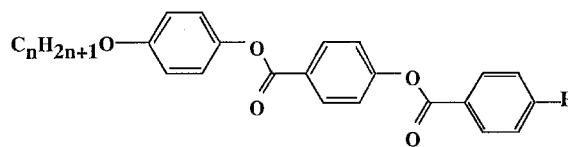
In earlier papers [7, 8], we reported that in 4-alkoxy-phenyl 4-(4-*R*-benzoyloxy)benzoate systems the formation of the smectic A (SmA) phase is strongly dependent on the electrostatic nature of the substituent *R*; see table 1 for the 4-octyloxyphenyl system.

The smectic A-nematic (isotropic) transition temperatures show a significant substituent effect, while the clearing point for the trifluoromethyl derivative is similar to those for the other derivatives. The hydrogen, methoxy, and methyl compounds of the octyloxy homologues are nematogenic, and the virtual smectic A-nematic (SmA-N) transition temperature extrapolated from the binary phase diagrams is very low. In this connection,

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† Part I see ref. [7].

Table 1. Transition temperatures (°C) for 4-octyloxyphenyl 4-(4-*R*-benzoyloxy)benzoates



<i>R</i> ( <i>n</i> = 8)	Cr	SmA	N	I
H	•	118	[45] <sup>a</sup>	• 135 •
CH <sub>3</sub>	•	112		• 189 •
OCH <sub>3</sub>	•	101		• 214 •
F	•	114	• 122	• 185 •
Br	•	128	• 192	• 222 •
CF <sub>3</sub>	•	128	• 210	• •
CN <sup>b</sup>	•		200	• 240 •

<sup>a</sup> Brackets indicate a virtual transition temperature extrapolated from the binary phase diagram [7].

<sup>b</sup> See [8].

the methoxy and methyl groups have a negative  $\sigma_p^+$  value [9], and their electron-donating nature would increase the polarity of the adjacent carboxyl group. On the other hand, halogen, trifluoromethyl, and cyano substituted compounds show the SmA as well as the N phase. These substituents have a positive  $\sigma_p^+$  value, and their electron-withdrawing nature could decrease the polarity of the adjacent carboxyl group. These facts

indicate that the electrostatic nature of the terminal substituent is the important factor for determining smectic properties. In these derivatives, the smectic properties of the trifluoromethyl compound are noteworthy, since the ratio of the SmA–N to N–I transition temperatures is the largest of all [10]. The remarkable smectic properties of the trifluoromethyl compound might be difficult to explain in terms only of the electrostatic nature of the terminal trifluoromethyl group.

In this paper, we describe a further examination of the liquid crystalline properties of the homologous series of 4-alkoxyphenyl 4-(4-trifluoromethylbenzoyloxy)benzoates (**1**), and discuss the effect of the trifluoromethyl group on the thermal properties of the liquid crystalline phases.

## 2. Experimental

### 2.1. Materials

The homologues of **1** were prepared by the conventional method with 4-trifluoromethylbenzoic acid and the corresponding 4-(4-alkoxyphenoxycarbonyl)phenols [7]. The purity of the materials was checked by HPLC, <sup>1</sup>H NMR spectroscopy, and DSC using a 'DSCPURITY' program (Seikodenshi Co.); purity was better than 99%.

### 2.2. Method

Transition temperatures and latent heats were determined using a Seiko SSC-5200 differential scanning calorimeter with indium (99.9%) as calibration standard; the DSC thermogram was operated at a heating or cooling rate of 5°C min<sup>-1</sup>. 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 with a Rigaku-denki RINT 2200 diffractometer with CuK<sub>α</sub> (λ = 1.543 Å) as an X-ray source, the temperature being controlled by a Rigaku PTC-20A thermo-controller. The reflection angle 2θ was calibrated by comparison of both

left and right reflections. The powdered sample packed into a quartz capillary (1.5 mm diam.) was heated to the isotropic state, and the measurement carried out during the cooling process.

## 3. Results and discussion

### 3.1. Thermal properties

The transition temperatures and latent heats for the compound **1** homologues are summarized in table 2.

As mentioned above, the octyloxy homologues of the hydrogen, methyl, and methoxy compounds are nematogenic, and the virtual SmA–N transition temperatures are very low [7]. In contrast, only the methoxy, ethoxy, propoxy, and butoxy homologues of **1** show the N phase, with a narrow temperature range. The SmA phase, with a focal-conic fan texture under homogeneous alignment, commences from the ethoxy homologue; the pentyloxy and later homologues show only the SmA phase. These results indicate that the liquid crystal core involving the terminal trifluoromethyl group intrinsically favours the layer arrangement.

The ethoxy and later homologues also show another kind of smectic phase (S) with a broken focal-conic fan texture. This smectic phase has an optically uniaxial nature. The latent heats for the S–SmA transition are higher than those for the SmA–N and N–I transitions, indicating that the smectic phase has a higher order of molecular arrangement.

Figure 1 shows transition temperatures plotted against the number of carbon atoms in the alkoxy chain.

In the present compounds, interestingly, the melting points of the homologues display a good even–odd alternation (except for the methoxy homologues) where the melting points for the even members are higher than those for the odd ones. The results indicate that the packing of the terminal group is also important in determining the thermodynamic properties of the crystalline phase, similarly to the nematic phase.

Table 2. Transition temperatures and latent heats for compounds **1**.

n	Cr	Transition temperature/°C					Latent heat/kJ/mol						
		S	SmA	N	I	ΔH <sub>Cr-S</sub>	ΔH <sub>S-SmA</sub>	ΔH <sub>SmA-N/I</sub>	ΔH <sub>N-I</sub>				
1	•	231	—	—	•	233	•	36.8			0.6		
2	•	191	(•	181) <sup>a</sup>	•	209	•	228	•	28.0	20.0	2.1	0.9
3	•	147	•	165	•	214	•	215	•	9.8	21.8	3.5	1.2
4	•	154	(•	142)	•	217	•	217	•	21.9	22.6		5.4 <sup>b</sup>
5	•	130	(•	123)	•	215	—	•	•	17.8	12.3	5.5	
6	•	135	(•	120)	•	214	—	•	•	33.5	11.6	5.7	
7	•	128	(•	118)	•	211	—	•	•	39.5	7.1	6.7	
8	•	128	(•	118)	•	210	—	•	•	41.8	12.1	6.7	

<sup>a</sup> Parentheses indicate a monotropic transition.

<sup>b</sup> The total for the SmA–N and N–I transitions.

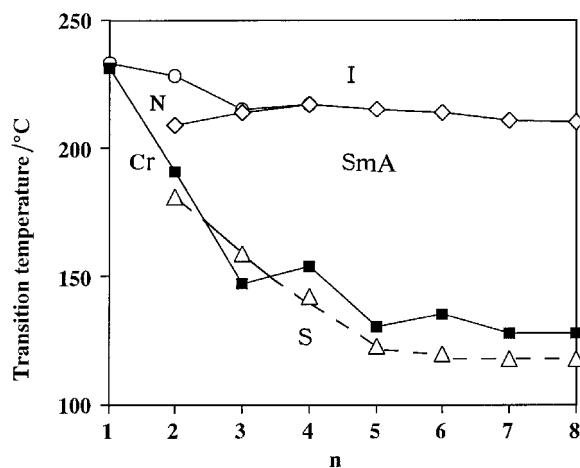


Figure 1. Plots of transition temperatures against number of carbons in the alkoxy chain,  $n$ . Cr, S, SmA, N, and I indicate crystal, unidentified smectic, smectic A, nematic, and isotropic phases, respectively. Dashed line indicates a monotropic transition. Transitions: ■ Cr-S/SmA/N, △ S-SmA, ◇ SmA-N/I, ○ N-I.

Occurrence of the S phase commences from the ethoxy homologue; the S-SmA transition temperatures fall steeply and become constant along the melting point on ascending the series. This indicates that the S and crystalline (Cr) phases have similar thermodynamic properties.

A thermodynamic characteristic of the present system is that the SmA-N(I) transition temperatures are almost independent of the number of carbon atoms in the alkoxy chain, despite the high clearing points (200°C, on average). This fact indicates that the interactions around the core group involving the terminal trifluoromethyl group are dominant in determining the thermal stability of the SmA phase, overcoming a disadvantageous factor due to increase in flexibility around the long alkoxy chain.

The N-I transition temperature appears to fall, while displaying a weak even-odd alternation, on ascending the series, while the N phase is formed in only four homologues.

### 3.2. X-ray examination of the smectic phases

The X-ray profiles of the SmA phase show a sharp reflection at 3–4° arising from the smectic layer ( $d_{001}$ ) and a broad one at  $c. 20^\circ$  arising from the molecular distance within the layer ( $d_{100}$ ). The X-ray data for the  $d_{001}$  reflection are summarized in table 3. In the table, the molecular lengths for the most stable conformation were calculated by an AM1 method (MOPAC ver. 6.0).

The layer spacings are always larger than the calculated molecular lengths, and the ratio of the layer spacing to the molecular length becomes small on ascending the series, indicating that the SmA phase has a

Table 3. Layer spacings ( $d$ ) and molecular lengths ( $l$ ) for compounds 1.

$n$	Layer spacings/Å <sup>a</sup>	Molecular lengths/Å <sup>b</sup>	$\Delta l/\text{Å}$	$d/l$
2	24.4	22.0	2.4	1.09
3	25.3	23.1	2.2	1.09
4	26.5	24.4	2.1	1.09
5	27.9	25.7	2.0	1.09
6	28.9	26.8	2.1	1.09
7	30.1	28.1	2.3	1.08
8	31.5	29.2	2.3	1.08

<sup>a</sup> The layer spacings were obtained at  $T_{\text{SmA}}$  or  $T_{\text{SmA-I}}-10^\circ\text{C}$ .

<sup>b</sup> Molecular lengths were estimated by molecular orbital calculations (see text).

so-called ‘partially bilayer arrangement’ of the molecules. Interestingly, the differences between the layer spacing and the molecular length are  $c. 2 \text{ Å}$ , which is close to the longitudinal length of the trifluoromethyl group.

In figure 2, the layer spacings and calculated molecular lengths are plotted against the number of methylene carbons ( $n$ ) in the alkoxy group. Although the plot of the calculated molecular length against  $n$  shows some ruggedness due to a weak even-odd effect, it can be approximated to a straight line, giving the slope of 1.27 Å per methylene unit. Similarly, the slope of the plot for the layer spacing against  $n$  gives a slope of 1.29 Å per methylene unit. These results indicate that the average longitudinal axis of the alkoxy group in the SmA phase is almost perpendicular to the smectic plane.

The X-ray profile for the S phase of the propoxy homologue is shown in figure 3. A sharp and weak reflection arising from the layer is observed at 3.52° (25.1 Å) arising from the  $d_{001}$  reflection, which is shorter than that of the SmA phase. The profile also shows two sharp and intense reflections at 19.44° (4.56 Å) and 21.0° (4.22 Å), with some weak reflections at 20.10° (4.41 Å),

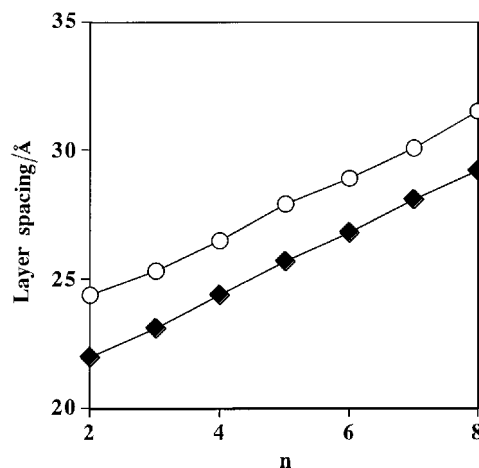


Figure 2. Plots of layer spacings (○) for the SmA phase and calculated molecular lengths (◆) against  $n$ .

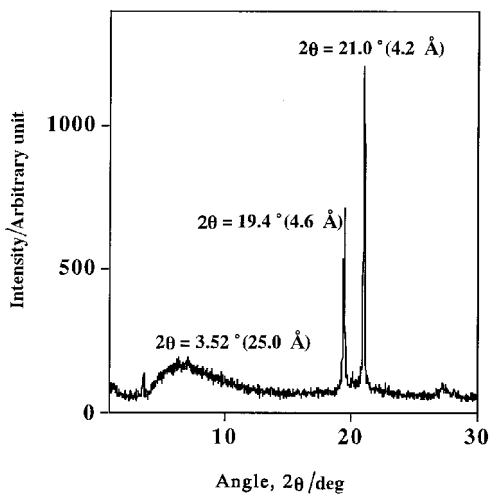


Figure 3. X-ray profile for the S phase of the propoxy homologue of compounds **1** at 155°C.

7.00° (12.6 Å), amongst others. Further analysis of the profile was impossible because of the un-oriented sample; however, there is no doubt that the S phase has a highly ordered arrangement of the molecules within the smectic layer just as a smectic B or an E phase.

### 3.3. Molecular arrangements in smectic and crystalline phases

As mentioned above, the layer spacings in the SmA phase are always 2 Å longer than the calculated molecular lengths. From these results, two critical arrangement models for the propoxy homologue are proposed, see figure 4. In the models, the layer spacings for both arrangements are *c.* 2 Å longer than the calculated molecular length. It would be reasonable to assume that in asymmetric liquid crystals the molecules are apt to arrange antiparallel on average, on the requisites of dipole correlation and minimized molecular volume.

In model A, the trifluoromethyl groups are arranged outside of the smectic layer, and meet around the boundary of the smectic layers, where the alkoxy chains are surrounded by aromatic moieties or *vice versa*. The relative arrangement of the functional groups does not change even in the higher homologues. The interlayer fluorophilic interaction around the layer boundary would effectively facilitate the formation and stabilization of the layer structure.

In model B, on the other hand, the trifluoromethyl groups are placed inside of the smectic layer and are surrounded by the long hydrocarbon chains. In this circumstance the fluorophobic interaction between the trifluoromethyl group and hydrocarbon moieties might be unfavourable for maintaining the layer structure. However, the terminal atoms of the hydrocarbon chains meet and form the smectic layer, similarly to liquid

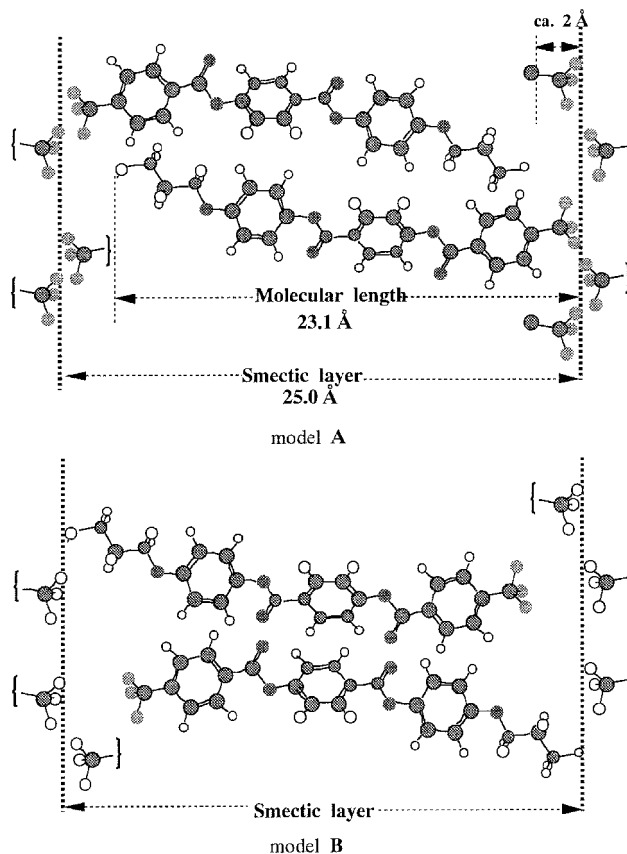


Figure 4. Possible molecular arrangements in the smectic phases.

crystals with alkyl groups at both terminals. Although the liquid crystalline cores appear to arrange closely and antiparallel in the models, the distance between adjacent liquid crystalline cores in practice is a function of the terminal alkoxy chain length, so that the overlap of the cores becomes progressively less with increasing alkoxy chain length. In this case, the attractive electrostatic interaction around the core groups involving dipoles in the antiparallel arrangement would become weaker on ascending the homologous series.

As shown in figure 1, in practice, the SmA–N and SmA–I transition temperatures are almost independent of the alkoxy chain length, whilst the S–SmA transition and melting temperatures fall steeply and become constant. As a result, the phase diagrams of the smectic and crystalline phases show features similar to each other but different from those of the SmA phase, indicating that the molecular interactions maintaining the crystalline and smectic phases are different from those for the SmA phase.

The abnormal stability (see table 1) and phase behaviour (figure 1) for the SmA phase imply the important influence of the terminal trifluoromethyl group on thermodynamic properties. In order to demonstrate effectively

the fluorophilic interaction around the trifluoromethyl groups, the model A arrangement should be the most suitable.

On the other hand, the S–SmA transition temperatures fall steeply, along with the melting points, with increasing hydrocarbon chain length. This indicates that the attractive interactions maintaining the crystalline and smectic structures rapidly weaken on ascending from the methyl to propyl groups, and the phases have a similar molecular arrangement to each other. In addition, the melting points of the trifluoromethyl compounds are similar to those of the methyl, methoxy and halogenated compounds, as shown in table 1. These results indicate that the electrostatic interactions around the core groups are more important for the thermodynamic properties of the S and crystalline phases than are the specific interactions around the terminals as in model A. Therefore, we assume that the S and Cr phases have a structure similar to model B, where the electrostatic interactions around core groups, resulting from the closest packing of the core groups, is the primary influence on thermodynamic properties. An important fact is that in model B the overlap of the core group would become less on ascending the homologues, so that the thermal stabilities of these phases would fall. X-ray examination has indicated that the single crystal of the propoxy homologue has a similar structure to model B [11]. Of course, crystal structure is strongly dependent on the alkoxy chain length, so that every homologue does not necessarily have a structure similar to the model.

Conclusively, in the present system a large molecular rearrangement takes place during the crystal (smectic)–smectic A and smectic A–smectic transitions, where the fluorophilic interaction around the terminal trifluoromethyl groups effectively determines the thermodynamic properties of the SmA phase. In this connection, the terminal trifluoromethyl group must also affect the

thermodynamic properties of the nematic phase, as mentioned by Gray *et al.* [3].

It is already known that polar liquid crystals such as nitro or cyano derivatives have specific thermodynamic properties resulting from polar interactions directed along the longitudinal axis of the liquid crystalline core. However, table 1 indicates that the halogenated and trifluoromethyl compounds have distinct SmA properties, unlike the alkyl and alkoxy compounds, despite the general concept that lateral short range interactions around the long alkyl group are of primary importance for layer formation. These results indicate that inter-layer interactions around the boundary of the smectic layer as well as lateral short range interactions are also important for the phenomena.

Further examination of the smectic properties of liquid crystals having an asymmetric structure is now in progress.

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