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The preparation and thermal properties of homologous series of 4-alkoxyphenyl 3-fluoro- and 3-methyl-4-thiocyanatophenyl terephthalates are described. Both homologous series show nematic phases; smectic A and C phases are also formed in the higher homologous. The methyl group and fluorine atom adjacent to the thiocyanate group lower the clearing points, in comparison with the unsubstituted compounds. The layer structures for both smectic A and C phases were characterized by X-ray diffraction experiments. The effects of the substituents on liquid crystalline properties are discussed.
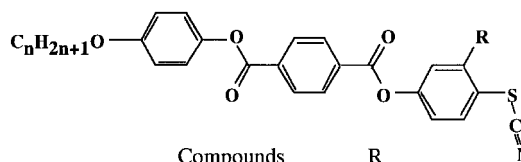
1. Introduction

It is well known that liquid crystals having a cyano group at the terminal position show interesting poly-mesomorphic behaviour, including a re-entrant nematic and several smectic A phases, where the large dipole moment along the longitudinal direction of the molecule is supposed to play an important role [1]. The cyanato and thiocyanato groups are particularly interesting terminal substituents in this respect. It is known that the cyano groups in these moieties at the terminal position have bent angles of *c.* 80° and 70° for –S–CN and –O–CN to the long axis, respectively.

Recently, some liquid crystalline materials having the –SCN [2–5], –OCN [6] and –CH₂CN [7] groups at the terminal position were prepared, and it has been clarified that the 'bent' cyano group affects the mesomorphic and dielectric properties differently from the 'longitudinal' cyano group.

In an earlier paper, for example, we reported that a homologous series of 4-thiocyanatophenyl 4-(4-alkoxy-benzoyloxy)benzoates show smectic A phases having a partially bilayer arrangement of molecules, in a similar way to polar liquid crystals [4]. On the other hand, some members of 4-alkoxyphenyl 4-thiocyanatophenyl terephthalates (3) show a smectic B phase, unlike polar liquid crystals, in addition to the nematic and smectic A phases [4]. In these homologues the terminal thiocyanato group would rotate freely at the liquid crystalline temperature, so that the average dipole moment arising from

the polar group is parallel to the longitudinal axis of the liquid crystalline core, similar to the situation with terminal cyano compounds. The introduction of a substituent at the position adjacent to the thiocyanato group is expected to impede rotation and induce a lateral dipole moment.

This paper describes the preparation and the thermal properties of homologous series of 4-alkoxy-phenyl 3-fluoro-(1) and 3-methyl-(2)4-thiocyanatophenyl terephthalates. The experimental results are discussed in terms of the molecular structure.

Compounds	R
1	F
2	CH₃
3	H

2. Experimental

2.1. *Materials*

2.1.1. *3-Fluoro-4-thiocyanatophenol*

The introduction of a thiocyanato group into the aromatic ring has previously been achieved by the reaction of phenol and ammonium thiocyanate in methanol [8]. In the present work, a convenient new method has been developed, as shown below.

A solution of ammonium thiocyanate (10.3 g, 0.134 mol) and *N*-chlorosuccinimide (19.4 g, 0.134 mol)

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in methanol (150 ml) was stirred for 1.5 h at 0°C. To this solution, 3-fluorophenol (5 g, 0.05 mol) in methanol (20 ml) was added dropwise, and the resulting mixture stirred for 24 h at room temperature. The reaction mixture was poured into a 20% sodium carbonate solution (100 ml), and the product extracted with ether (4 × 50 ml). The crude product was purified by column chromatography on silica gel, followed by recrystallization from a mixed solvent of ether and hexane, giving 3-fluoro-4-thiocyanatophenol as colourless needles, 1.17 g (20%), m.p. 55°C. The purity was checked by differential scanning calorimetry (DSC) using a DSCPURITY program (Seiko Denshi). IR: 2172 cm^{-1} (v_{CN}). ^{1}H NMR (δ): 5.10 (1H, s), 6.70–6.75 (2H, m), and 7.44 (1H, d, $J = 8.5$ Hz) ppm.

One isomer was obtained in the crude extract, indicating that the reaction is highly selective.

2.1.2. *3-Methyl-4-thiocyanatophenol*

The introduction of the thiocyanato group into a 3-substituted phenol is strongly dependent on the electrostatic nature of the substituent. A similar treatment (as above) of 3-methylphenol gave 3-methyl-4-thiocyanato-phenol, yield > 70%, m.p. 76°C. IR: 2162 cm^{-1} (v_{CN}). ^{1}H NMR (δ): 2.49 (3H, s), 5.88 (1H, s), 6.71 (1H, dd, 8.6 and 3.0), 6.80 (1H, d, 3.0), and 7.47 (1H, d, $J = 8.6$ Hz) ppm.

The homologues of **1** and **2** were obtained by the following scheme, making use of syntheses of 4-alkoxyphenyl hydrogen terephthalic acids and an esterification procedure described in an earlier paper [9].

2.2. *Characterization*

IR spectroscopy was performed on a Horiba FT-200 infrared spectrometer. ^{1}H NMR spectra were recorded with a Nihon-Denshi EX-270 spectrometer in deuterated chloroform solution. Transition temperatures and latent

heats were determined using a Seiko SSC-5200 DSC, with indium (99.9%) as a calibration standard (m.p. 156.6°C, 28.4 J g^{-1}). Liquid crystal phase textures were observed using a Nikon POH polarizing microscope fitted with a Mettler FP-900 thermo-control system.

X-ray diffraction experiments were performed using a Rigaku-denki RINT 2200 diffractometer with CuKα ($l = 1.542$ Å) as an X-ray source. The reflection angle (2θ) was calibrated by both left and right examination, and the temperature of the sample was controlled by a Rigaku PTC-20A thermo-controller. The powdered sample, loaded into a quartz capillary (diameter 1.5 mm), was heated to the isotropic temperature, and the measurement carried out during cooling.

3. Results and discussion
3.1. *Thermal properties*

Transition temperatures and latent heats for series **1** and **2** compounds, are summarized in the table.

The SmA phase shows focal conic fan and homeotropic textures under homogeneous and homeotropic alignments, respectively. On the other hand, the SmC phase shows broken focal conic and schlieren textures under homogeneous and homeotropic alignments, respectively. The SmC–SmA transition temperatures for **1g** and **1h** were determined by observation under the microscope since the phase transition was not detectable by DSC thermogram. In an earlier paper, compounds **3** had been reported to show a smectic B (SmB) phase having a broken focal conic fan texture with optically uniaxial nature [9]. However, the SmB phase was not observed in **1** and **2** compounds.

Figure 1 gives plots of transition temperature against the number of atoms in the alkoxy group. For comparison, transition temperatures for the corresponding unsubstituted thiocyanato compounds (**3**) are also given.

The introduction of a fluorine atom or methyl group at the position adjacent to the thiocyanato group reduces
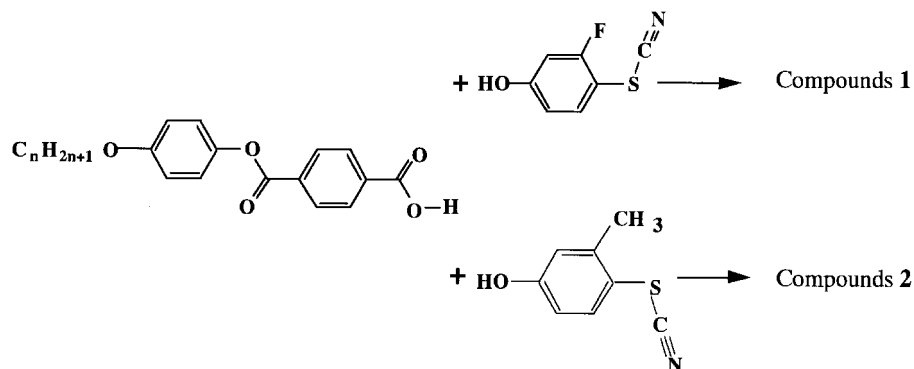
Scheme.

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

Compound	n	Cr		SmC		SmA		N		I	C–N or SmC	SmC–SmA or N	SmA–N	N–I
1a	1	•	149	—		—		•	165	•	38.5			0.1
1b	2	•	139	—		—		•	166	•	19.7			0.3
1c	3	•	149	—		—		•	152	•	39.8			0.2
1d	4	•	128(	•	106)	—		•	153	•	34.4	0.3		0.3
1e	5	•	122(	•	115)	—		•	152	•	23.9	0.2		0.3
1f	6	•	105	•	116	•	120	•	151	•	20.8	0.1	0.1	0.2
1g	7	•	101	•	117	•	127	•	154	•	21.3	1[a]	0.2	0.3
1h	8	•	104	•	109	•	138	•	156	•	24.6	1[a]	0.2	0.7
1i	9	•	101	•	101	•	150	•	157	•	41.3	1[a]	0.3	0.5
2a	1	•	153	—		—		—		•	49.2		3.5	
2b	2	•	129	—		•	116	—		•	49.1		2.7	
2c	3	•	132(	•	73)	•	112	—		•	36.5	0.1	2.5[b]	
2d	4	•	101(	•	84)	•	115	•	117	•	31.3	0.1	2.0[b]	
2e	5	•	108(	•	80)	•	114	•	116	•	51.6	0.1	2.5[b]	
2f	6	•	108(	•	79)	•	113	•	115	•	38.0	0.1	2.6[b]	
2g	7	•	111(	•	75)	•	113	•	116	•	42.3	0.2	2.6[b]	
2h	8	•	112(	•	74)	•	117	•	118	•	43.8	0.2	2.8	
2i	9	•	97	—		•	123	•		•	41.5			

[a] The latent heat was too small to calculate.
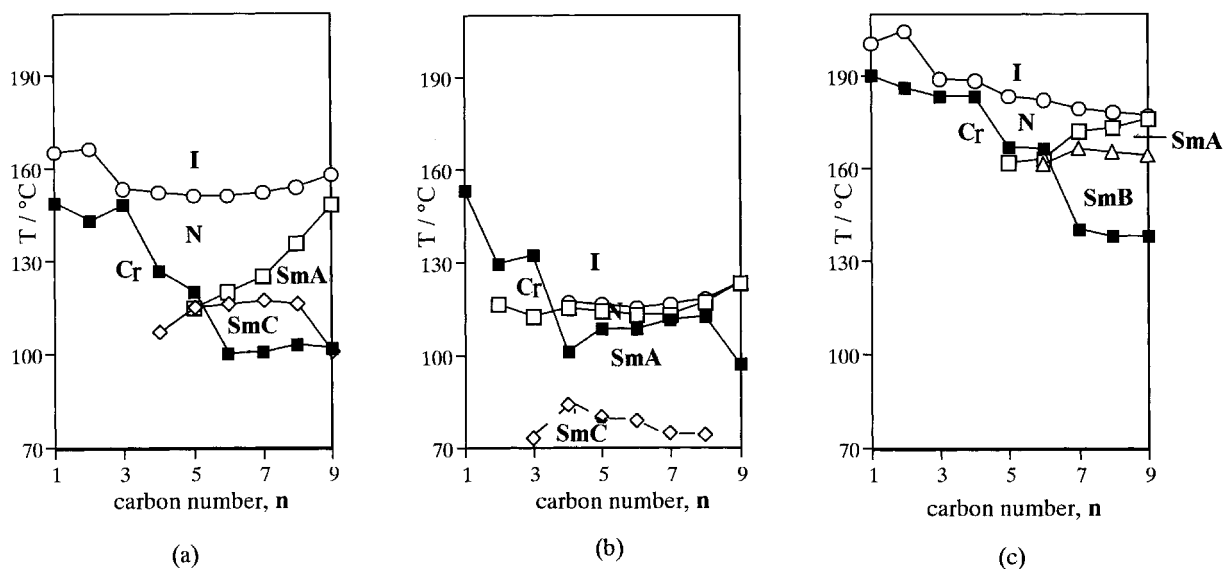[b] Sum of SmA–N and N–I transitions.

Figure 1.   Plots of transition temperatures against carbon number (n) for: (a); series **1**, (b); series **2**, and (c); series **3**. C, N, SmA, SmC, SmB, and I indicate crystal, nematic, smectic A, smectic C, smectic B, and isotropic phases, respectively. The dashed line indicates a monotropic transition.

the liquid crystal properties, in a similar way to other liquid crystalline materials. The influence of lateral substitution on the mesomorphic properties of compounds **1**–**3** can be expressed, for example for the octyloxy homologues, by the following orders of increasing clearing temperature (T_{cl}), nematic range (ΔT_N), smectic A transition temperature (T_{SmA}) (for SmA–N, I) and smectic A range (ΔT_{SmA}), depending on the lateral substituent R (see the table and [4]).

$n = 8$

T_{cl} R: $CH_3 < F < H$

ΔT_N R: $CH_3 < H < F$

T_{SmA} R: $CH_3 < F < H$

ΔT_{SmA} R: $CH_3 = H < F$

These results show that lateral methyl substitution in the present system produces liquid crystals with narrowest N and SmA ranges, having the lowest thermal stabilities; lateral fluoro substitution gives liquid crystals with the broadest mesophase ranges, exhibiting moderate thermal stabilities.

Interestingly, the orders of increasing clearing temperatures and SmA thermal stabilities, dependent on lateral substituents R, are opposite to the order of increase of their van der Waals radii [10]: H < F < CH₃. Another noteworthy fact is that the N–I transition temperatures for series **1** and **2** tend to increase towards highest n, giving minima for **1f** and **2f**. The fluorine atom apparently increases the nematic range, while the methyl group notably decreases it. Simultaneously, the methyl group lowers the SmC–SmA transition temperature. These facts indicate that the effect of these substituents on the mesomorphic properties are subtly different from each other. In addition, both substituents result in the disappearance of the SmB phase formed by series **3** compounds and facilitate the formation of the SmC phase.

These results can be summarized by the following orders of increasing T_{cl}, ΔT_N, T_{SmA}, and ΔT_{SmA} for the present system, showing the influence of the lateral substitution on the mesogenic efficiency of the alkoxy chain:

$R = H$

T_{cl} $C_9H_{19}O < C_8H_{17}O < C_7H_{15}O$
$< C_6H_{13}O < C_5H_{11}O < C_4H_9O$

ΔT_N $C_9H_{19}O < C_4H_9O = C_8H_{17}O$
$< C_7H_{15}O < C_6H_{13}O = C_5H_{11}O$

T_{SmA} $C_7H_{15}O < C_8H_{17}O < C_9H_{19}O$

ΔT_{SmA} $C_9H_{19}O < C_8H_{17}O < C_7H_{15}O$

$R = F$

T_{cl} $C_6H_{13}O < C_5H_{11}O < C_4H_9O$
$< C_7H_{15}O < C_8H_{17}O < C_9H_{19}O$

ΔT_N $C_9H_{19}O < C_8H_{17}O < C_4H_9O$
$< C_7H_{15}O < C_5H_{11}O < C_6H_{13}O$

$T_{SmA}, \Delta T_{SmA}$ $C_6H_{13}O < C_7H_{15}O < C_8H_{17}O$
$< C_9H_{19}O$

$R = CH_3$

T_{cl} $C_6H_{13}O < C_5H_{11}O = C_7H_{15}O$
$< C_8H_{17}O < C_9H_{19}O$

ΔT_N $C_9H_{19}O < C_8H_{17}O < C_4H_9O$
$= C_5H_{11}O = C_6H_{13}O < C_7H_{15}O$

T_{SmA} $C_7H_{15}O = C_6H_{13}O < C_5H_{11}O$
$< C_4H_9O < C_8H_{17}O < C_9H_{19}O$

ΔT_{SmA} $C_7H_{15}O < C_8H_{17}O = C_6H_{13}O$
$< C_5H_{11}O < C_4H_9O < C_9H_{19}O$

The SmA results presented show that lateral substitution of the present system affects the mesogenic efficiency of its alkoxy chain in varying degrees, depending on the nature of the lateral substituent R. Similar tends have been found for other liquid crystalline systems [11].

3.2. *X-ray diffraction examination*

In order to characterize the smectic phases, X-ray diffraction studies were carried out; the X-ray profiles for compound **1g** are shown in figure 2.

1g has the phase behaviour of a Cr–(SmC)–SmA–N–I type liquid crystal. The X-ray profile at 130°C (N) shows
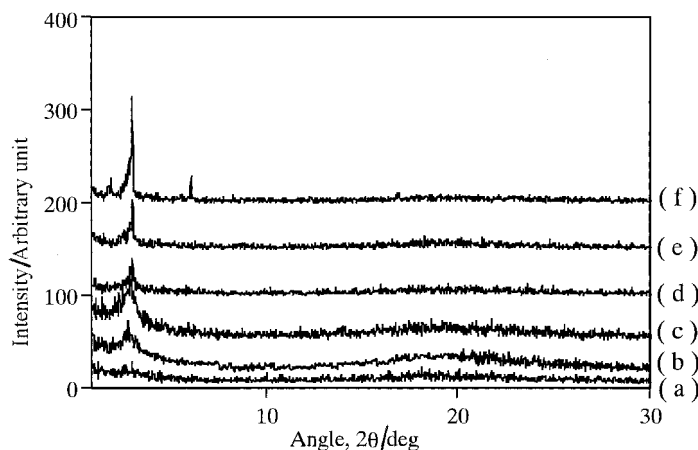

Figure 2. X-ray profiles for compound **1f**. (*a*) 130°C (N), (*b*) 118°C (SmA), (*c*) 114°C (SmC), (*d*) 111°C (SmC), (*e*) 108°C (SmC), (*f*) 100°C (SmC).

two broad reflections at 15°–25° and 2.6°–3.0°. The former reflection corresponds to 5.9–3.6 Å and arises from the average lateral distance of molecules (d_{100}). The latter reflection corresponds to 34–29 Å and arises from the smectic layer (d_{001}). As shown in figure 2, the reflection peak observed in the small angle region is very broad and weak in the N phase, indicating that a cybotactic group with the layer structure of the SmA phase is present.

The reflection in the small angle region gradually becomes sharp and intense with reducing temperature, and shows a maximum at 2.86° (30.9 Å) at 118°C (SmA). In the SmC phase the reflection maximum has a weak dependency on temperature; that is, 2.94° (30.0 Å) at 114°C, 3.04° (29.0 Å) at 111°C, 3.06° (28.9 Å) at 105°C and 3.06° (28.9 Å) at 100°C. The profile at 100°C (SmC) shows two sharp reflections at 3.06° (28.9 Å) and 6.10°

(14.5 Å), where the latter is assumed to be a second order reflection of the former. The weak temperature dependency arises from the change in the tilt angle.

3.3. *Molecular orbital calculation*

In order to clarify the conformation around the thiocyanato group, the rotational barrier was estimated by calculation with an AM1 method (MOPAC, Ver. 6.0). In our earlier paper, we described that in the most stable conformation from compounds **3** the thiocyanato group lies besides the aromatic ring, due to the π-π interaction between the aromatic ring and the cyanato group. While the rotational barrier around the phenyl–SCN bond is very small (1.0 kJ mol^{-1}), so that the thiocyanoto group would rotate almost freely at the liquid crystal temperature, the coplaner conformation must be preferentially present in the LC [4, 9].
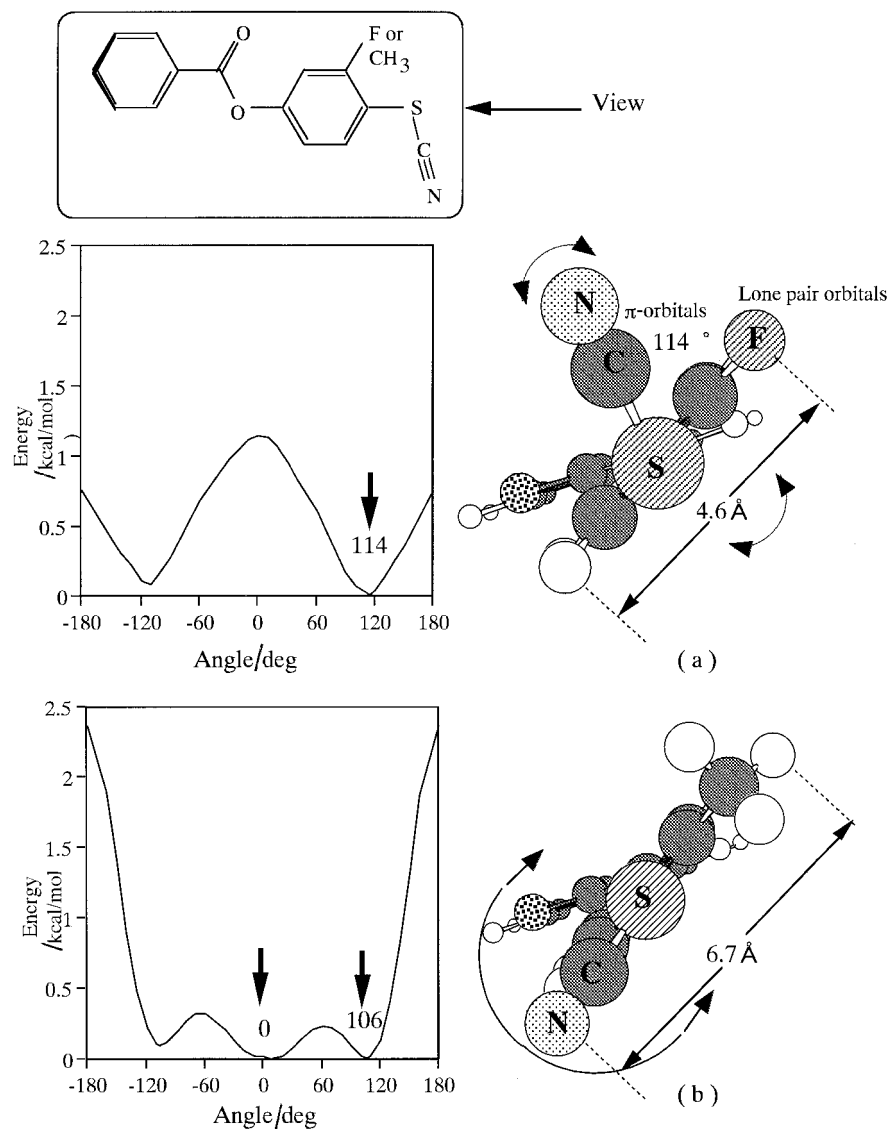

Figure 3. Rotational energy diagrams for: (*a*) 4-thiocyanato-3-fluorophenyl benzoate, (*b*) 4-thiocyanato-3-methylphenyl benzoate. The values were calculated by an AM1 method (MOPAC ver. 6.0).

A fluorine atom is known to have a van der Waals radius of 1.35 Å, and the C–F bond is *c.* 1.34 Å. These values are slightly larger than for hydrogen, so the introduction of the fluorine atom at a lateral position of a liquid crystalline core would increase the breadth. In addition, the electrostatic interaction between the fluorine atom and thiocyanato group is assumed to play an important role in determining the conformation. In the present calculation, 3-fluoro-4-thiocyanotophenyl benzoate was used as a model compound, and in figure 3 the rotational barrier is plotted against the rotational angle.

As shown in figure 3(*a*), the rotational barrier of the thiocyanoto group for compounds **1** is minimized for the staggered conformation with a twist angle of 114°, where the attractive interaction between the π orbitals of the thiocyanoto group and the σ orbitals of the fluorine atom stabilizes the conformation. The two staggered conformations should be evenly distributed at any temperature, though free rotation must be maintained, since the energy difference between the most stable and unstable conformations is only 1.2 kcal mol^{-1}. In such circumstances, it would be reasonable to assume that the fluorine atom does not significantly increase the molecular breadth.

From figure 3(*b*), on the other hand, the rotational barrier for compounds **2** is determined only by the steric hindrance between the thiocyanato and methyl groups, and the rotational barrier of 2.4 kcal mol^{-1} is far larger than that for **1**. This rotational barrier of 2.4 kcal mol^{-1} is almost comparable to that of an *n*-alkane (*c.* 3 kcal mol^{-1}). Therefore, we conclude that the thiocyanato group should be located in the range indicated by arrow in figure 3(*b*), although the rotation of the thiocyanato group is maintained at liquid crystal temperatures. In addition, the methyl group adjacent to the thiocyanato group significantly increases the molecular breadth due to steric hindrance.

The average N–I transition temperatures for series **1**, **2** and compounds **3** (from the butoxy to octyloxy homologues) are 153, 116, 182°C, respectively. The difference may be attributed to the geometrical difference between their substituents. As can be seen from figure 1(*b*), compounds **2** with the large molecular breadth favour the SmA phase, rather than the N phase where the polar interaction around the terminal group stabilizes the layer structure (see below).

The molecular lengths of compounds **1** were calculated according to conformational information, and the results are plotted against the number of carbons in figure 4. In this figure, the layer spacings for the SmC and SmA phases obtained from X-ray experiments are also indicated.

The layer spacings for the SmA phase of compounds **1** monotonously increase on ascending the series, being
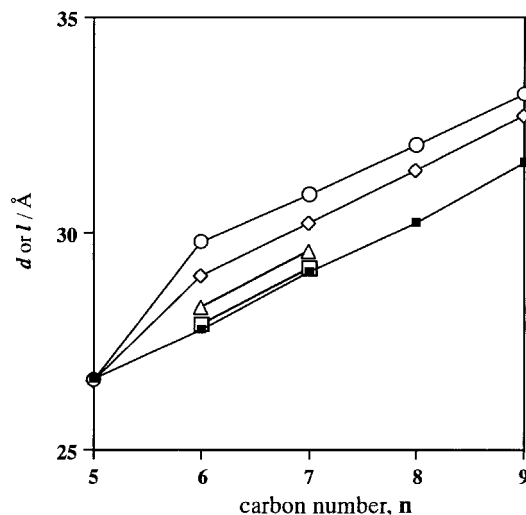

Figure 4.   Plots of calculated molecular lengths (*l*) and layer spacings (*d*) of series **1** and **2** compounds. ○ layer spacing of SmA phase for **1**, ◇ layer spacing of SmC phase for **1**, △ layer spacing of SmA phase for **2**, □ layer spacing of SmC phase for **2**, ■ calculated molecular length. The layer spacings for the SmA and SmC phases were taken at $T_{SmA–N}$-5 and $T_{SmC–SmA}$-5°C, respectively, except for **1f** (at 118°C).

1.05–1.07 times larger than the calculated molecular lengths, indicating that the molecules form so-called 'partially bilayer' arrangement. Thus, the layer spacings are always *c.* 3 Å longer than the calculated molecular lengths. Interestingly, the excesses roughly agree with the longitudinal length of the thiocyanato group. In the SmC phase, the layer spacings are also longer than the calculated molecular lengths, and shorter than those of the SmA phase. In general, the difference between the layer spacings of the SmA and SmC phases is attributed to the reduction of the layer spacing due to the tilt of the liquid crystal core. A simple calculation [cos^{-1} (ratio of the layer spacing of the SmC phase to the SmA phase)] from figure 3 gives a tilt angle of *c.* 10° for the SmC phase.

The SmA and SmC phases for compounds **2** commence from the hexyloxy and pentyloxy homologues, respectively. The layer spacings for the SmA phase of **2** are 0.7–1.0 Å longer than the calculated molecular lengths, indicating that these molecules also form the partially bilayer arrangement. Interestingly, the layer spacing for the SmC phase of the pentyloxy homologue exactly agrees with the calculated molecular length, indicating that the SmC phase also has the partially bilayer arrangement.

Figure 5 shows a possible molecular arrangement for the SmA phase of **1f**, where the layer spacing obtained by X-ray experiment and molecular length calculated by the AM1 method are 29.8 and 26.8 Å, respectively. It
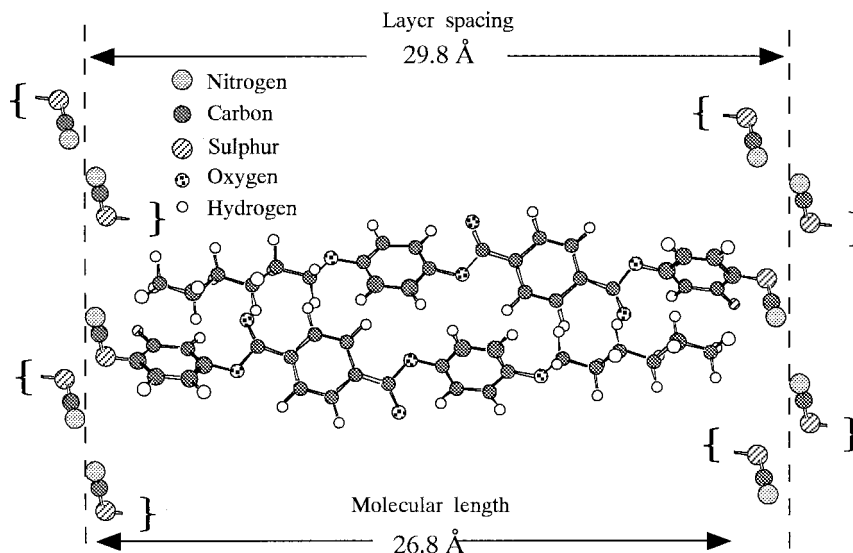
Figure 5. Molecular arrangement model for the SmA phase of compound **1f**.

would be reasonable to assume that the polar molecules arrange antiparallel on average within the layer. The terminal thiocyanato groups are placed around the boundaries of the smectic layer, and produce a relatively polar space. In the model, the excess of 3 Å roughly agrees with the longitudinal length of the thiocyanato group; the dipole–dipole interaction around the thiocyanato groups between the layers may facilitate the arrangement. Some polar liquid crystals having a cyano or a nitro group at the longitudinal position have been known to form antiparallel dimers due to the strong polar interactions, giving rise to the formation of the SmA_α phase [1]. However, the polarity of the thiocyanato group may not be strong enough to form tight antiparallel dimers.

4. Conclusion

In the present compounds, the introduction of a fluorine atom or methyl group adjacent to the thiocyanato group causes the disappearance of the SmB phase, gives rise to the formation of the SmC phase, and leads to a reduction in the thermal stability of liquid crystal phases. The SmA and SmC phases form the partially bilayer arrangement, where the polar interlayer interactions around the layer boundary are likely to facilitate the layer arrangement.

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