

Design of Liquid Crystals with “de Vries-Like” Properties: Organosiloxane Mesogen with a 5-Phenylpyrimidine Core

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Ferroelectric liquid crystals (FLC) have generated a considerable amount of research activity over the past 30 years, ranging from fundamental studies on the molecular origins of spontaneous polar ordering to the commercial development of high-resolution reflective liquid-crystal-on-silicon (LCOS) microdisplays with switching times in the range of microseconds.^{1,2} Materials used in FLC microdisplay applications are normally composed of an achiral liquid crystal mixture with an isotropic–nematic–smectic A–smectic C (INAC) phase sequence and a chiral dopant that induces a ferroelectric polarization P_S in the tilted smectic C phase. Coupling of P_S to an applied electric field enables switching of the ferroelectric SmC* phase between opposite tilt orientations, thereby producing an ON–OFF light shutter between crossed polarizers.³ One major problem in formulating FLC mixtures for display devices is the layer contraction caused by the tilting of molecules upon transition from the orthogonal SmA phase to the SmC phase (Figure 1a), which results in a buckling of the smectic layers into a chevron geometry and the formation of “zigzag” defects that reduce the optical quality of the FLC film.⁴

To solve this problem, several groups have focused on a class of liquid crystals characterized by layer contractions on the order of $\leq 1\%$ at the SmA–SmC phase transition.^{5–15} The structure of the SmA phase formed by these unusual materials (so-called “de Vries-like”) has yet to be fully elucidated,¹⁶ although recent theoretical studies suggest that calamitic materials combining low orientational order and high lamellar order are likely to exhibit this behavior.^{17,18} This is consistent with the fact that most “de Vries-like” materials feature nanosegregating structural elements such as siloxane end-groups or partially fluorinated side-chains that strongly promote lamellar order.¹⁴ Examples of such materials include **3M 8422** and **TSiKN65**, which show layer contractions of ca. 0.4 and 0.65%, respectively.^{6,7}

There is currently no rational design strategy for liquid crystals with “de Vries-like” properties. However, we have recently shown that combining a structural element that promotes the formation of a SmC phase (trisiloxane-terminated side-chain) with one that promotes the formation of a SmA phase (chloro-terminated side-chain)¹⁹ in a mesogen with a 2-phenylpyrimidine core results in a maximum layer contraction of 1.6%.²⁰ This is significantly smaller than the layer contraction of 7.1% observed with the parent compound **PhP1**,²¹ which may reflect a frustration between the SmA- and SmC-promoting elements in **1**. To test this hypothesis, and validate our design strategy for “de Vries-like” liquid crystals, we designed another trisiloxane-terminated mesogen in which the SmA-promoting element is a nonplanar 5-phenylpyrimidine core (2).²² In this Communication, we report the synthesis and charac-

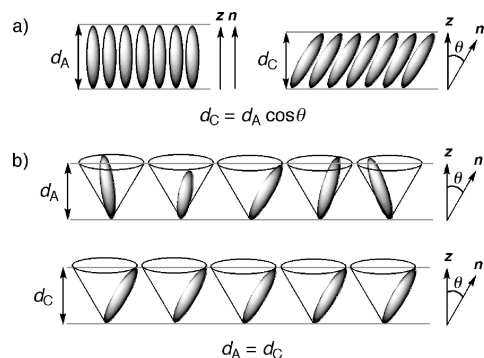


Figure 1. Schematic representations of the SmA–SmC phase transition according to (a) a classic rigid-rod model and (b) the diffuse cone model proposed by de Vries.¹⁶

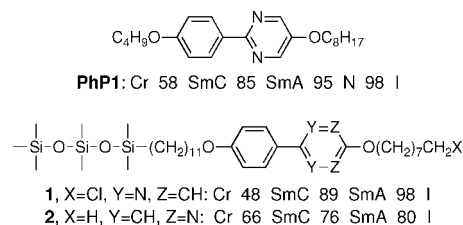


Figure 2. Phenylpyrimidine mesogens and their phase transition temperatures (°C) measured by DSC on heating.

terization of this new material, which is comparable to the best “de Vries-like” liquid crystals reported heretofore.^{6,7}

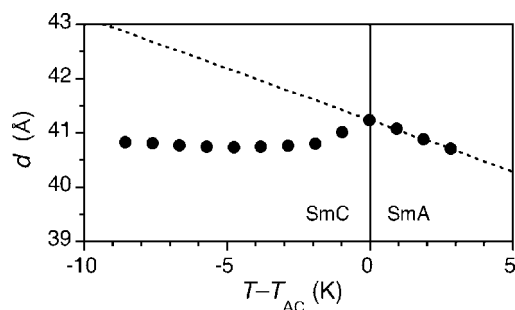
Compound **2** was obtained by conversion of 2-chloro-5-(4-methoxyphenyl)pyrimidine²³ to 5-(4-methoxyphenyl)-2-(1-octyloxy)pyrimidine by a nucleophilic aromatic substitution reaction, followed by selective demethylation using NaSEt and alkylation via a Mitsunobu reaction with 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol (Supporting Information). The mesophases formed by compound **2** were characterized by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Compound **2** forms both SmA and SmC phases, as shown by the characteristic fan and homeotropic textures of the SmA phase that turn into broken fan and Schlieren textures upon transition to the SmC phase. Accurate measurements of the smectic layer spacing (d) as a function of temperature were carried out by small-angle X-ray scattering (SAXS). As shown in Figure 3, the layer spacing d in the SmA phase increases with decreasing temperature, which is likely due to an increase in orientational order, and in effective molecular length as the alkyl side-chains become more extended at lower temperature.⁶ Other “de Vries-like” materials have been reported to show a similar negative thermal expansion in their $d(T)$ profiles.¹⁴ Upon SmA–SmC phase transition, the layer spacing decreases from 41.2 Å to a minimum value of 40.7 Å, which

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Table 1. Smectic Layer Spacings, Tilt Angles, and Figures of Merit R and f at $T - T_{AC} = -10$ K

cpd	d_c (Å)	d_A (Å)	$d(T_{AC})$ (Å)	θ_{opt} (deg)	θ_{Xray} (deg)	δ (deg)	R	f
PhP1 ^a	24.8	26.0	25.9	21	17.5	16.8	0.80	0.83
1 ^b	47.7	49.4	48.5	24	15.1	10.4	0.43	0.63
2	40.8	43.1	41.2	35	18.8	8.0	0.23	0.54
3M 8422 ^c	31.7	32.3	31.8	25	11.0	4.5	0.18	0.44
TSiKN65 ^d	35.70	35.95	35.95	34	6.8	6.8	0.20	0.20

^a From ref 21. ^b From ref 20. ^c Estimated from data reported in ref 6.^d Estimated from data reported in ref 7 at $T - T_{AC} = -7$ K.**Figure 3.** Smectic layer spacing d as a function of reduced temperature $T - T_{AC}$ for compound **2**. The dashed line corresponds to the least-squares fit of the data points at $T - T_{AC} \geq 0$ K.

corresponds to a maximum layer contraction of 1.2%. The fan/broken fan texture of **2** observed by POM shows a pronounced change in interference color upon cooling from the SmA to the SmC phase, which is consistent with the increase in orientational order associated with a “de Vries-like” transition (Supporting Information).¹⁴

To assess the potential of a material to achieve a defect-free bookshelf geometry in the SmC phase, Radcliffe et al. defined the figure of merit R as the ratio of the “chevron layer tilt angle” $\delta(T)$, which is the tilt angle required to give the layer contraction relative to $d(T_{AC})$ at the SmA–SmC transition temperature, over the optical tilt angle $\theta_{opt}(T)$ measured by POM (eq 1).⁶ According to this expression, a material would approach the idealized bookshelf geometry as $R \rightarrow 0$. They also defined an expression for de Vries character that takes into account negative thermal expansion (eq 2), where the “X-ray tilt angle” $\theta_{Xray}(T)$ is the tilt angle required to give the layer contraction relative to $d_A(T)$ extrapolated into the SmC phase according to a least-squares fit of the data in the SmA phase (dashed line in Figure 3). Measurements of θ_{opt} as a function of temperature were carried out by POM using a mixture of **2** doped with a chiral additive (3 mol%) in a 5 μ m ITO glass cell with rubbed Nylon alignment layers (Supporting Information).

$$R = \delta(T)/\theta_{opt}(T) = \cos^{-1}[d_C(T)/d(T_{AC})]/\theta_{opt}(T) \quad (1)$$

$$f = \theta_{Xray}(T)/\theta_{opt}(T) = \cos^{-1}[d_C(T)/d_A(T)]/\theta_{opt}(T) \quad (2)$$

As shown in Table 1, the optical tilt angle θ_{opt} of **2** is ca. twice as large as the X-ray tilt angle θ_{Xray} , which is consistent with “de Vries-like” behavior. To put these results in perspective, we calculated R and f values at a reduced temperature $T - T_{AC} = -10$ K for **1**, **2** and PhP1,^{20,21} and for 3M 8442 and TSiKN65 (Table 1).^{6,7} The R and f values for **2** are lower than those obtained for **1**, despite showing comparable layer contractions, which is due in part to the greater tilt angle θ_{opt} formed by **2**. When compared to

the parent compound PhP1, the R and f values for both **1** and **2** clearly support our hypothesis that combining structural elements promoting SmA and SmC phases in a single molecule increases de Vries character. In terms of the potential to achieve a defect-free bookshelf geometry, the R value of compound **2** is comparable to those of 3M 8422 and TSiKN65, which are considered to be among the best “de Vries-like” materials.¹⁴ A detailed study of organosiloxane mesogens featuring the 5-phenylpyrimidine core is under way to broaden the temperature range of the SmC phase formed by such material, and assess their electro-optical properties in FLC display devices.

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Supporting Information Available: Synthesis of compound **2**, DSC and POM characterization, and plots of θ_{Xray} and θ_{opt} vs $T - T_{AC}$ for compounds **1**, **2**, and PhP1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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