

Directed Metalation Route to Ferroelectric Liquid Crystals with a Chiral Fluorenol Core: The Effect of Restricted Rotation on Polar Order

J. Adam McCubbin,[†] Xia Tong,[‡] Ruiyao Wang,[†] Yue Zhao,[‡] Victor Snieckus,^{*†} and Robert P. Lemieux^{*†}

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6, and Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

Received October 7, 2003; E-mail: lemieux@chem.queensu.ca; snieckus@chem.queensu.ca

Abstract: A new series of smectic C* (SmC*) mesogens containing a chiral (*R*)-2-octyloxy side chain and either a fluorenone (**2a–e**) or chiral fluorenol (**3a–e**) core were synthesized using a combined directed *ortho* metalation–directed remote metalation strategy. The SmC* phase formed by the fluorenol mesogens is more stable and has a wider temperature range than that formed by the fluorenone mesogens, which may be ascribed to intermolecular hydrogen bonding according to variable-temperature FT-IR measurements. The C₁₁ fluorenol mesogens (*R,R*)-**3d** and (*S,R*)-**3d** were obtained in diastereomerically pure form and gave reduced polarization (*P*₀) values of +106 and +183 nC/cm², respectively, at 10 K below the SmA*–SmC* phase transition temperature. The difference in *P*₀ values suggests that the chiral fluorenol core contributes to the spontaneous polarization of the SmC* phase. This is ascribed to the bent shape of the fluorenol core, which should restrict its rotation with respect to the side chains in the SmC* phase and favor one orientation of its transverse dipole moment along the polar axis, and to steric coupling of the core to the chiral 2-octyloxy side chain.

Introduction

The design of molecules forming liquid crystal phases has evolved considerably over the past 30 years. The discovery of new mesophases and the development of detailed structure–property relationships have opened new and exciting opportunities—as well as challenges—for organic and organometallic chemists. The term “liquid crystal” is often associated with nematic liquid crystals, which are used in the ubiquitous flat panel LCDs, although two-dimensionally ordered smectic liquid crystals are far more diverse than nematics and offer a wider range of potential applications.¹ Chiral smectic C* (SmC*) liquid crystals have played a key role in the commercial development of high-resolution reflective microdisplays by virtue of their bistability, fast electrooptical switching, and wide viewing angle; these materials also hold tremendous potential in nonlinear optic and photonic applications.² In the SmC* phase, rod-shaped chiral molecules (mesogens) formed by a rigid aromatic core and two

paraffinic side chains are organized in diffuse layers. Within each layer, molecular long axes are uniformly tilted at an angle θ with respect to the layer normal. In a surface-stabilized planar alignment (Figure 1), SmC* liquid crystals are ferroelectric; i.e., they possess a bulk electric polarization (spontaneous polarization, *P*_S) along a polar axis perpendicular to the plane defined by the molecular long axis *n* and the layer normal *z* (tilt plane).³ This spontaneous polarization allows switching of the FLC between opposite tilt orientations by applying an electric field across the film.⁴

Understanding the relationship between molecular structure and the magnitude of *P*_S is essential to the development of useful SmC* liquid crystal materials for NLO and photonics applications.² The spontaneous polarization is a chiral bulk property originating from a conformational preference of transverse molecular dipoles to orient in one direction along the polar axis because of steric coupling between polar functional groups and the stereogenic center(s) in the SmC* mesogens (stereopolar coupling). Empirical and semiempirical structure–property relationships based on conformational analysis of such stereopolar units are well established for SmC* mesogens with chiral side chains, although far less is known in the case of SmC* mesogens with chiral cores.^{5–7} Recent work on SmC* liquid crystals induced by nonmesogenic dopants with chiral biphenyl cores has shown that the induced polarization varies significantly

[†] Queen's University.

[‡] Université de Sherbrooke.

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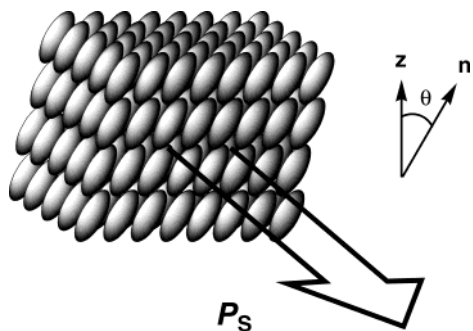


Figure 1. Schematic representation of the SmC* phase in a planar alignment.

with the structure of the achiral SmC host, and is highest when the SmC host has a complementary core structure that enables the dopant to exert a strong chiral perturbation on surrounding host molecules.⁸ This unusual manifestation of molecular recognition via core–core interactions is seldom observed when the stereogenic center is located in the side chain because of the higher degree of conformational disorder in paraffinic structures which precludes effective molecular recognition between dopant and host.⁹ In this paper, we extend the concepts of molecular recognition and self-assembly in the SmC* phase to include intermolecular hydrogen-bonding interactions and report on a new class of SmC* mesogens with chiral fluorenol cores.

Noncovalent interactions such as van der Waals forces and hydrogen bonding play a key role in the formation and thermal stability of smectic liquid crystal phases. Over the past decade, work in the area of hydrogen-bonded liquid crystals has focused primarily on the self-assembly of complementary nonmesogenic units via intermolecular hydrogen bonding to give rod- and disklike supramolecular structures that form stable liquid crystal phases.^{10,11} Earlier work in this area has focused on the stabilizing effect of intermolecular hydrogen bonding on the liquid crystal phases of single compounds. Examples of compounds which self-assemble via “head-to-head” hydrogen bonding to form smectic phases (Figure 2a) include 4-alkoxybenzoic acids,¹² *trans*-4-alkoxycinnamic acids,¹³ bolaamphiphiles,¹⁴ and amphiphilic carbohydrates.¹⁵ Lateral hydrogen bonding (Figure 2b) has also been shown to enhance positional ordering and

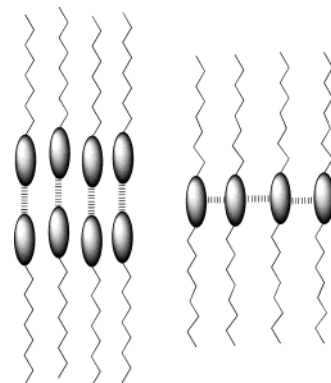


Figure 2. Schematic representations of (a) “head-to-head” hydrogen bonding (left) and (b) lateral hydrogen bonding (right).

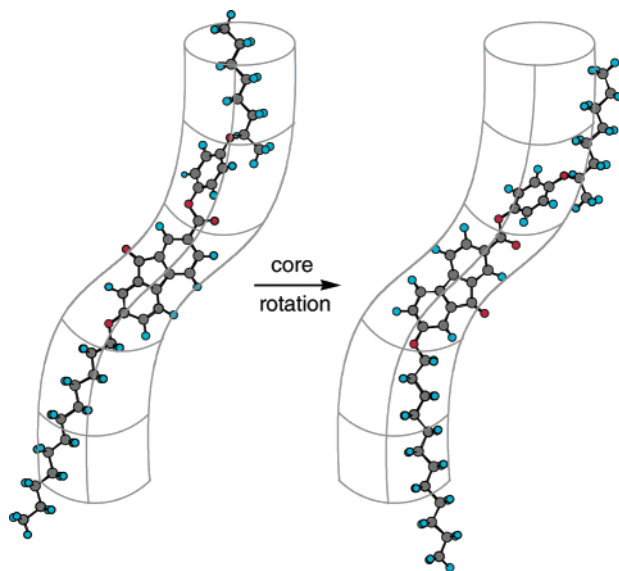


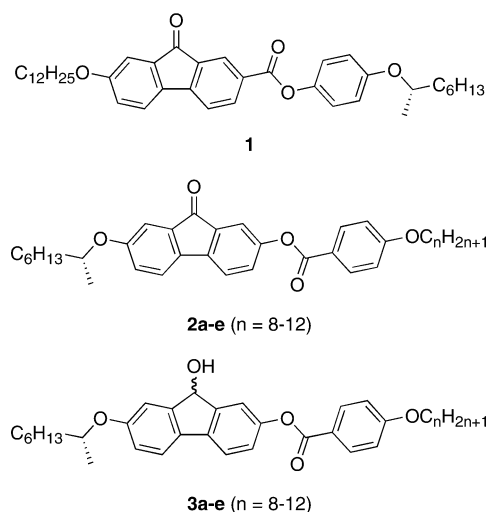
Figure 3. Molecular models (MM2) of mesogen **1** in relation to the mean-field potential (*binding site*) which models the conformational and orientational ordering imposed by the SmC* phase according to the Boulder model.²¹ From left to right, the fluorenone core is rotated 180° with respect to the two side chains.

thus promote the formation of smectic phases.¹⁶ In general, these hydrogen bond interactions take place between rigid mesogenic cores, and they must be strong enough to counterbalance any unfavorable steric repulsion caused by lateral functional groups acting as hydrogen bond donor and/or acceptor.¹⁷

Mesogens with a chiral fluorenol core can be derived from unsymmetrically disubstituted fluorenones and provide an excellent opportunity to study the effect of lateral hydrogen bonding on polar ordering in an SmC* phase. There are only a few examples of fluorenone liquid crystals in the literature,^{18–20} including compound **1**, which forms an enantiotropic SmC* phase between 81 and 123 °C and gives a moderate spontaneous polarization of ca. +50 nC/cm².²⁰ Interestingly, mesogens with fluorenone or fluorenol cores should be conformationally more restricted than conventional mesogens with biphenyl cores in the SmC* phase. The fluorenone/ol cores are bent and cannot freely rotate with respect to paraffinic side chains while maintaining the zigzag molecular shape imposed by the SmC* phase (Figure 3).²¹ Because of this rotational bias, the transverse dipole moment of a chiral fluorenol core should have a preferred orientation along the SmC* polar axis that depends on its absolute configuration, and should therefore contribute to the spontaneous

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polarization. To test this hypothesis, we designed the novel fluorenol mesogens **3a–e**, which are derived from the fluorenones **2a–e**.



There are two stereopolar units in **3** that can contribute to the spontaneous polarization: the conventional (*R*)-2-octyloxy side chain and the fluorenol core. In this design, the coupling of the 2-octyloxy side chain to the fluorenol core is intended to force these two stereopolar units to act cooperatively in producing a spontaneous polarization, and thus facilitate the assessment of core contribution to the spontaneous polarization by comparing P_S values for the (*R,R*) and (*S,R*) diastereomers of **3**. The presence of the 2-octyloxy side chain ensures that a measurable spontaneous polarization is indeed observed. In this paper, we report the syntheses of the mesogenic fluorenones **2a–e** and fluorenols **3a–e** as mixtures of (*R,R*) and (*S,R*) diastereomers, and of the fluorenols (*R,R*)- and (*S,R*)-**3d** in diastereomerically pure form, using a combined directed *ortho* metalation (DoM)–directed remote metalation (DreM) strategy. The results suggest that intermolecular hydrogen bonding stabilizes the SmC* phase formed by **3a–e** and that the chiral fluorenol core contributes significantly to the spontaneous polarization.

Results and Discussion

Synthesis. Several methods have been reported for the synthesis of substituted fluorenones, including Friedel–Crafts

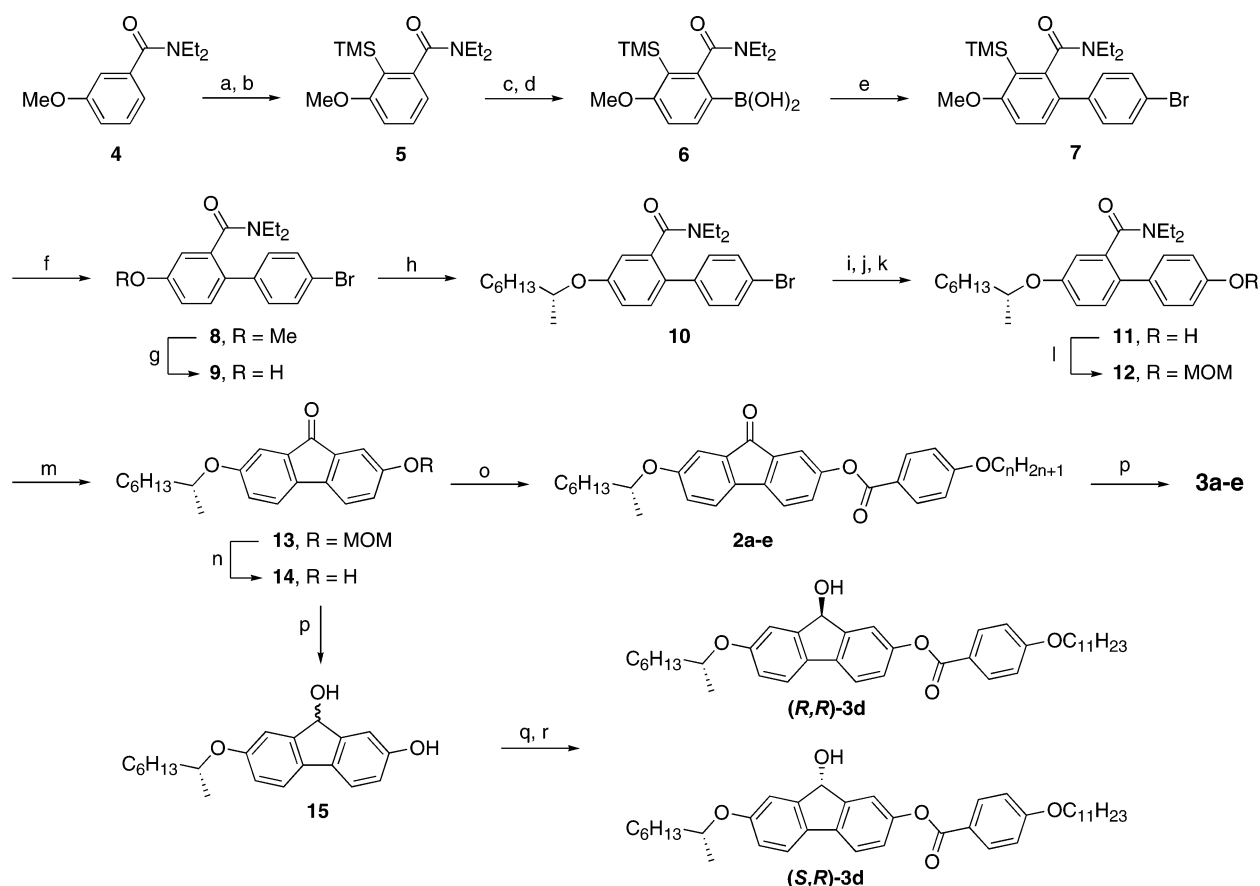
cyclization reactions,^{22,23} intramolecular cycloadditions of conjugated aryl enynes²⁴ and diynes,²⁵ and oxidation of fluorenones.^{26,27} Recent advances in transition-metal-catalyzed C–H bond insertion reactions have led to the development of palladium-catalyzed cyclizations of *o*-iodobenzophenones²⁸ and cyclocarbonylation of *o*-iodobiaryls.²⁹ However, difficulties in the synthesis of appropriate 2,7-disubstituted fluorenes or cyclization precursors to 2,7-disubstituted fluorenones prompted us to develop a different approach based on the DreM³⁰ of *o*-biarylcarboxamides derived from a combined DoM/cross-coupling strategy.

The fluorenones **2a–e** were obtained as mixtures of (*R,R*) and (*S,R*) diastereomers by sodium borohydride reduction of the corresponding fluorenones **2a–e**. The synthesis of the fluorenones began with *N,N*-diethyl-3-methoxybenzamide (**4**), which was metalated preferentially between the two directed metalation groups (DMGs) and quenched with trimethylsilyl chloride to give the TMS-protected benzamide **5** in 81% yield (Scheme 1). The second DoM step occurred selectively *ortho* to the stronger amide DMG, and the lithiated intermediate, upon quenching with B(OMe)₃ and hydrolysis, gave the boronic acid **6**. Interestingly, reaction of the crude **6** with a variety of protected 4-iodophenols under Suzuki–Miyaura cross-coupling conditions gave homocoupling products. As an alternative, 4-bromoiodobenzene was used as coupling partner, with the intention of subsequent replacement of the bromo function by an alkoxy group. Suzuki–Miyaura cross-coupling was achieved regioselectively to give the biphenyl **7** in 70% overall yield from **5**. Removal of the TMS group with TBAF, and demethylation with BBr₃, gave the hydroxybiphenyl **9** in 75% yield. The chiral (*R*)-2-octyloxy side chain was introduced via a Mitsunobu inversion reaction to give **10** in 93% yield and >99% ee according to chiral stationary phase HPLC analysis (Daicel Chiralpak-AS, 2% IPA/hexanes). Subsequent conversion of the Br group to OH was achieved via lithium–halogen exchange followed by trapping with B(*O*-*i*-Pr)₃ and peroxide oxidation to give **11** in 88% yield. Protection of the OH group as a methoxymethyl ether (94%) proved necessary for the subsequent DreM to take place. Hence, cyclization of **12** was achieved by treatment with 5 equiv of LDA at 0 °C, followed by warming to room temperature to give the fluorenone **13** in 81% yield. After demomylation in quantitative yield, esterification of **14** with 4-alkoxybenzoic acids with alkyl chain lengths ranging from C₈ to C₁₂ using DCC gave a homologous series of five chiral fluorenone esters (**2a–e**) in 95–99% yields. Chemoselective reduction of **2a–e** with NaBH₄ gave the corresponding fluorenols **3a–e** as mixtures of diastereomers in 89–92% yields.

The synthesis of the fluorenol **3d** in diastereomerically pure form was achieved by an indirect route. Recently, Velasco et al. reported the asymmetric reduction of 1-substituted fluorenones with moderate enantioselectivities but in relatively poor yields.³¹ Given the small amounts of fluorenones available for

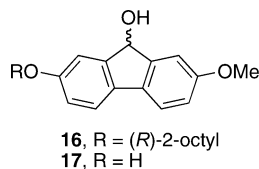
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Scheme 1^a

^a Reagents and conditions: (a) 1.25 M *s*-BuLi, TMEDA, THF, -78°C ; (b) (TMS)Cl, -78 to $+25^{\circ}\text{C}$, 81%; (c) 1.25 M *s*-BuLi, TMEDA, THF, -78°C ; (d) B(OMe)₃, -78 to $+25^{\circ}\text{C}$; (e) Pd(PPh₃)₄, 1 M aqueous K₂CO₃, 4-bromiodobenzene, DME, reflux, 70%; (f) TBAF, 25°C , THF, 92%; (g) BBF₃, CH₂Cl₂, -78 to $+25^{\circ}\text{C}$, 81%; (h) PPh₃, DIAD, CH₂Cl₂, (*S*)-2-octanol, 25°C , 93%; (i) 2.0 M *n*-BuLi, -78°C ; (j) B(O-*i*-Pr)₃, -78 to $+25^{\circ}\text{C}$; (k) 35% aqueous H₂O₂, 0°C , 88%; (l) (MOM)Cl, CH₂Cl₂, *i*-Pr₂NEt, 25°C , 94%; (m) 1.0 M LDA, THF, 0 to 25°C , 81%; (n) 6 M aqueous HCl, *i*-PrOH, 25°C , 99%; (o) DCC, DMAP, 4-alkoxybenzoic acid, CH₂Cl₂, 25°C , 95–99%; (p) NaBH₄, MeOH/Et₂O, 25°C , 89–92%; (q) semipreparative HPLC resolution, Daicel Chiralpak-AS column, 5% IPA/hexanes, 3.0 mL/min; (r) 1-(4-undecyloxybenzoyl)benzotriazole, 0.5 M aqueous NaOH, THF, 25°C , 72–80%.

asymmetric reduction, we attempted to resolve the diastereomers of **3a–e** by chiral stationary phase HPLC on three different columns (Regis Whelk-O 1, Daicel Chiralcel-OJ, and Chiralpak-AS), but without success. However, we were able to resolve the diastereomers of the fluorenediol **15** by semipreparative chiral stationary phase HPLC using a Daicel Chiralpak-AS column to give (*S,R*)-**15** and (*R,R*)-**15** in diastereomerically pure form (>99% de). Further investigation revealed that interaction of the fluorenediol moiety with the amylose carbamate CSP of the Chiralpak-AS column plays a key role in the resolution of **15**. For example, the fluorenediol derivative **16** cannot be resolved on the Chiralpak-AS, whereas the fluorenediol derivative **17** is



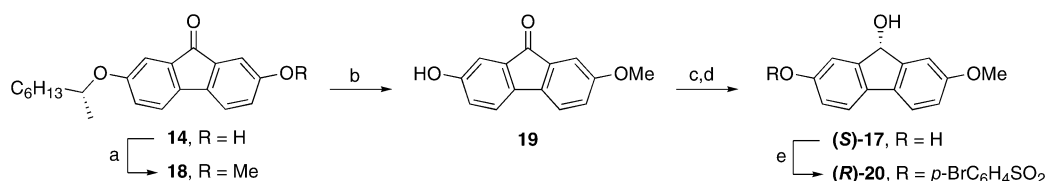
resolved with a higher efficiency than **15** under the same conditions (α values for **15** and **17** are 0.82 and 1.44, respectively). The resolved diastereomers (*R,R*)- and (*S,R*)-**15** were esterified selectively using 1-(4-undecyloxybenzoyl)triazole under

basic conditions³² to give the mesogens (*S,R*)-**3d** and (*R,R*)-**3d**, respectively.

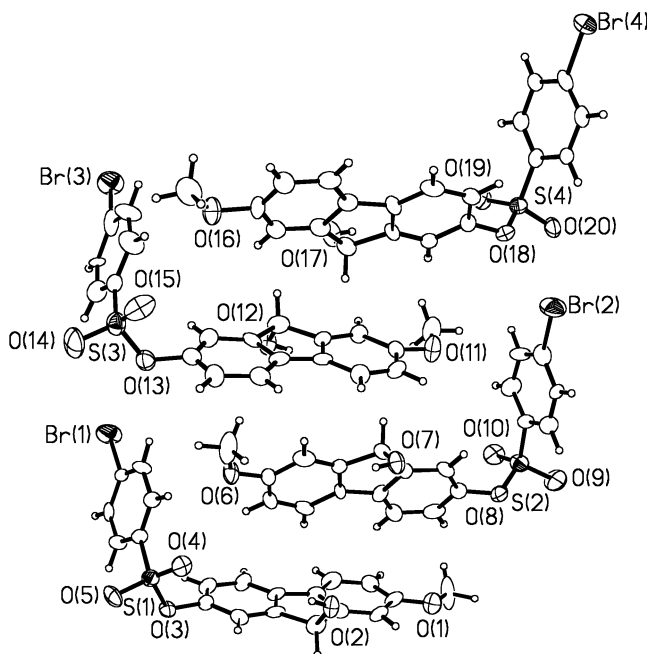
Recrystallization of the resolved fluorenediols (*R,R*)- and (*S,R*)-**15** and the mesogens (*R,R*)-**3d** and (*S,R*)-**3d** under a variety of conditions gave powdery solids that were unsuitable for X-ray crystallographic analysis. Several derivatives of **15**, including mono- and bis-4-bromobenzoates, 4-bromophenylsulfonates, 3,5-dinitrobenzoates, and triphenylsilyl ethers were synthesized in an attempt to produce crystals of suitable quality, but none of these compounds crystallized. Substitution of a methoxy group for the branched 2-octyloxy side chain significantly improved the crystallinity of the fluorenediol and made it possible to establish the absolute configuration of (*S,R*)-**15** indirectly on the basis of the reasonable assumption (*vide supra*) that the order of elution of the fluorenediol stereoisomers on the Chiralpak-AS column should be invariant of the nature of the alkoxy group at the 7-position. As shown in Scheme 2, the 7-methoxyfluorenediol **17** was derived from **14** in 43% overall yield and resolved by semipreparative CSP–HPLC, and the first eluant was converted to the *p*-bromophenylsulfonate **20**, which crystallized from 2:1 hexanes/CH₂Cl₂. The resulting crystal structure shown in Figure 4 establishes that the absolute configuration of the enantiomer of **17** first eluted from the Chiralpak-AS

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Scheme 2^a

^a Reagents and conditions: (a) MeI, K₂CO₃, CH₃CN, 95%; (b) 1.0 M BCl₃, CH₂Cl₂, -78 to +25 °C, 52%; (c) NaBH₄, MeOH, 25 °C, 88%; (d) semipreparative HPLC resolution, Daicel Chiralpak-AS column, 20% IPA/hexanes, 3.0 mL/min; (e) *p*-bromophenylsulfonyl chloride, 0.5 M aqueous NaOH, THF, 62%.

Figure 4. Crystal structure of (*R*)-20.

column is (*S*), and that the diastereomer of **15** first eluted from the same column is therefore (*S,R*).

Mesophase Characterization. The mesophases formed by compounds **2a–e** and **3a–e** were characterized by polarized microscopy, differential scanning calorimetry, and powder X-ray diffraction. The fluorenones **2a–e** form enantiotropic chiral nematic (N*) and SmC* phases over relatively narrow temperature ranges (Table 1). The disappearance of the N* phase with longer alkyl chain lengths is consistent with known empirical trends.³³ The corresponding fluorenols **3a–e** form enantiotropic SmC* phases only, except for **3b**, which also forms an unidentified higher order SmX phase. These SmC* phases occur over wider temperature ranges and have clearing points 30–34 K higher than those of the corresponding fluorenones, which is consistent with the stabilizing effect of lateral hydrogen bonding on smectic phase formation observed previously.¹⁶ Furthermore, the difference in clearing point between the resolved diastereomers suggests that this stabilizing effect is more pronounced in the case of (*R,R*)-**3d**. In all cases, the SmC* phase reappears on cooling from the isotropic or N* phase and persists all the way to room temperature. Texture analysis by polarized microscopy on unoriented thin films revealed the formation of broken fan textures with dechiralization lines which are characteristic of the SmC* phase (Figure 5).¹

Table 1. Liquid Crystalline and Ferroelectric Properties of Compounds **2a–e** and **3a–e**

| compd | n | phase sequence ^a | P _S ^b (nC/cm ²) | θ ^b (deg) | P _o ^b (nC/cm ²) |
|---------------------------|----|-------------------------------|--|-------------------------|--|
| 2a | 8 | Cr 74 (27.0) SmC* | +74 | 39 | +118 |
| | | 77 (2.6) N* 87 (1.0) I | | | |
| 2b | 9 | Cr 60 (34.5) SmC* | +77 | 39 | +122 |
| | | 83 (3.5) N* 87 (1.2) I | | | |
| 2c | 10 | Cr 58 (32.5) SmC* | +75 | 39 | +119 |
| | | 86 (5.9) N* 88 (0.4) I | | | |
| 2d | 11 | Cr 62 (35.0) SmC* | +70 | 39 | +111 |
| | | 87 (6.5) I | | | |
| 2e | 12 | Cr 70 (40.0) SmC* | +70 | 39 | +111 |
| | | 92 (9.7) I | | | |
| 3a | 8 | Cr 70 (23.3) SmC* | +67 | 33 | +123 |
| | | 116 (5.2) I | | | |
| 3b | 9 | Cr 74 (18.2) SmX* | +80 | 33 | +147 |
| | | 83 (5.1) SmC* | | | |
| 3c | 10 | Cr 74 (33.4) SmC* | +77 | 33 | +141 |
| | | 122 (7.6) I | | | |
| 3d | 11 | Cr 63 (32.8) SmC* | +70 | 33 | +128 |
| | | 120 (5.2) I | | | |
| 3e | 12 | Cr 65 (32.5) SmC* | +72 | 32 | +136 |
| | | 123 (8.5) I | | | |
| (<i>R,R</i>)- 3d | 11 | Cr 93 SmC* 128 I ^c | +58 | 33 | +106 |
| (<i>S,R</i>)- 3d | 11 | Cr 78 SmC* 120 I ^c | +100 | 33 | +183 |

^a Phase transition temperatures (°C) and enthalpies of transition (kJ/mol) (in parentheses) were measured on heating by differential scanning calorimetry at a rate of 5 K/min. ^b The spontaneous polarization (P_S), reduced polarization (P_o), and tilt angle (θ) values were measured at a reduced temperature of T - T_C = -10 K. ^c Phase transition temperatures measured by polarized microscopy.

Further analysis by variable-temperature powder X-ray diffraction confirmed the SmC* phase assignments. In each case, a single sharp Bragg peak was observed at small angles, with a broad halo at wide angles. The Bragg angle 2θ for the small angle peak remained constant over the temperature range of the SmC* phase. For the fluorenones **2a–d**, the small angle 2θ values range from 3.33° to 2.92°, which correspond to smectic layer spacings of 26.5–30.2 Å, respectively. The layer spacings are shorter than the calculated molecular lengths (34.0–37.6 Å), which is consistent with a tilted lamellar structure with tilt angles on the order of 37–39°. The small angle 2θ value for the fluorenone **3d** is 2.78°, which corresponds to a smectic layer spacing of 31.8 Å and a calculated tilt angle of 32.3°.

FT-IR Spectroscopy. To determine the nature and extent of hydrogen bonding in the SmC* phase formed by the fluorenone mesogens, FT-IR spectra of compound **3d** as a thin film were obtained as a function of temperature. In the crystalline phase at 35 °C, the spectrum shows a broad OH stretch band centered at 3310 cm⁻¹ and a single C=O stretch band at 1728 cm⁻¹, which suggests that the fluorenone OH groups are mostly self-associated via hydrogen bonding (Figure 6). Upon heating to the SmC* phase at 95 °C, a second C=O stretch band appears

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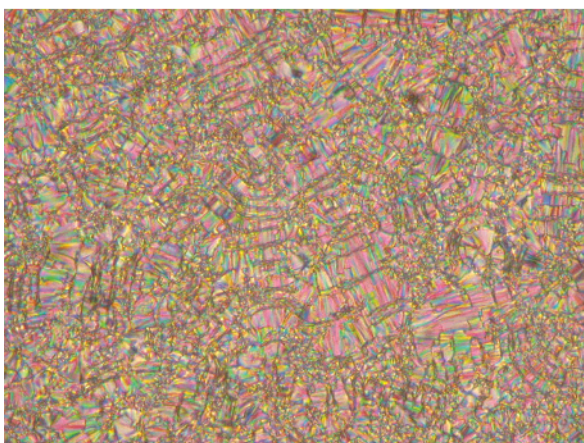
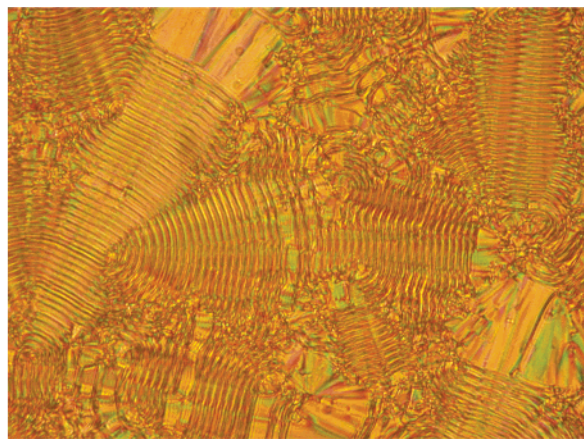


Figure 5. Polarized photomicrographs of **2d** (top) in the SmC* phase at 86 °C (500 \times) and **3d** (bottom) in the SmC* phase at 85 °C (400 \times).

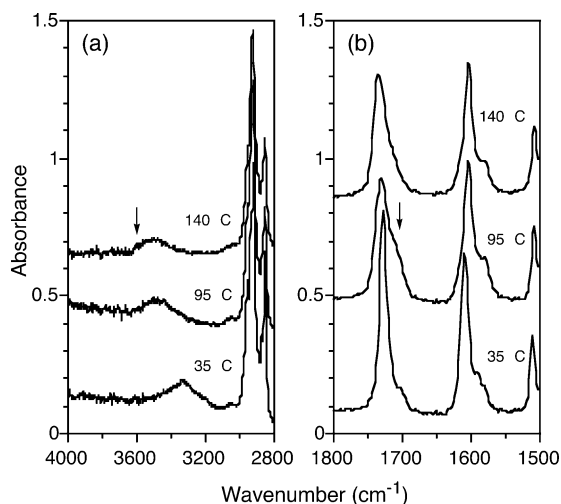


Figure 6. FT-IR spectra of **3d** as a thin film taken in the crystalline phase (35 °C), in the SmC* phase (95 °C), and in the isotropic liquid phase (140 °C).

at 1712 cm^{-1} (arrow in Figure 6b) and the OH stretch band is shifted toward higher frequencies (3484 cm^{-1}), which is consistent with the formation of hydrogen bonds between OH and C=O groups at the expense of OH self-association.³⁴ In the isotropic liquid phase at 140 °C, the intensity of the C=O

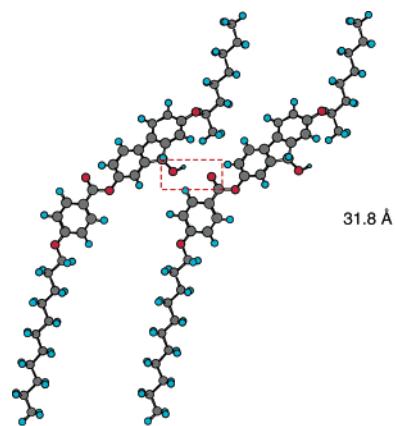


Figure 7. Molecular models (MM2) of **3d** in a tilted layer organization with a spacing of 31.8 Å. The rectangular box shows the hydrogen-bonded OH and C=O groups.

stretch band at 1712 cm^{-1} is diminished while the OH stretch band is shifted toward higher frequencies (3510 cm^{-1}), which is consistent with a decrease in the number of hydrogen bonds between C=O and OH. The appearance of a new band at ca. 3550 cm^{-1} , which corresponds to free OH groups, can also be distinguished (arrow in Figure 6a). These results are in agreement with a smectic layer model of **3d** showing the OH and C=O groups of neighboring molecules to be in close proximity when the molecules are in a tilted geometry with a layer spacing corresponding to that derived from the powder X-ray measurements (Figure 7). These results strongly suggest that intermolecular hydrogen bonding between the fluorenol core and the ester linking group is responsible for stabilizing the SmC* phase formed by **3a–e**.

Polarization Measurements. Spontaneous polarizations (P_S) and tilt angles (θ) were measured as a function of temperature for the mesogens **2a–e**, **3a–e**, (*R,R*)-**3d**, and (*S,R*)-**3d** as surface-stabilized 4 μm films. For comparison, the P_S and θ values measured at 10 K below the SmC*–N* or SmC*–I phase transition temperature ($T - T_C = -10$ K) are listed in Table 1 along with the corresponding reduced polarization values (P_o).³⁵ The tilt angles measured by polarized microscopy are in good agreement with those derived from X-ray diffraction measurements and found to be invariant with temperature. The P_o values for the fluorenones **2a–e** are ca. 10–20% higher than that reported for the fluorenone **1** (+105 nC/cm^2 at $T - T_C = -10$ K)²⁰ in which the 2-octyloxy side chain is decoupled from the fluorenone core. The positive sign of polarization is consistent with that reported for conventional SmC* mesogens bearing an (*R*)-2-octyloxy side chain, and can be rationalized by conformational analysis according to the Boulder model.²¹ The P_o values for the diastereomeric mixtures **3b–e** are ca. 20% higher than those obtained for the corresponding fluorenones **2b–e**, which suggests that the chiral fluorenol core makes an appreciable contribution to the spontaneous polarization.

This assertion is confirmed by comparing the polarizations of the resolved diastereomers (*R,R*)-**3d** and (*S,R*)-**3d** (Figure 8).

(35) According to phenomenological theory, the spontaneous polarization P_S and tilt angle θ of a SmC* phase are related to the reduced polarization P_o according to the equation $P_o = P_S/\sin \theta$. The reduced polarization is intrinsic to the chiral component of the SmC* phase at a fixed reduced temperature $T - T_C$. Kuczynski, W.; Stegemeyer, H. *Chem. Phys. Lett.* **1980**, *70*, 123.

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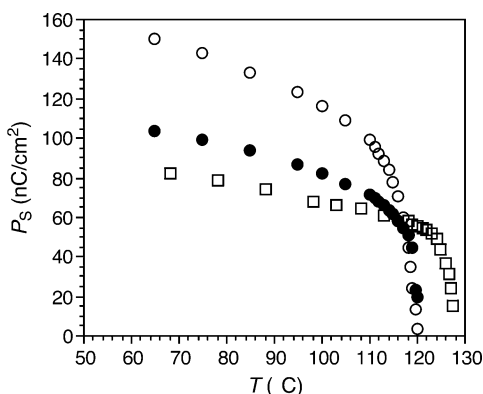


Figure 8. Spontaneous polarization P_s as a function of temperature T for the diastereomeric mixture **3d** (filled circles) and the resolved diastereomers (*R,R*)-**3d** (open squares) and (*S,R*)-**3d** (open circles).

The reduced polarization of conventional SmC* mesogens with an (*R*)-2-octyloxy side chain is normally on the order of +105 nC/cm² which is ca. 40% less than that measured for (*S,R*)-**3d**.³⁶ This suggests that the (*S*)-fluorenol core makes a significant contribution to the spontaneous polarization, and that its transverse dipole moment is oriented in the same direction along the polar axis as that of the (*R*)-2-octyloxy side chain. On the other hand, the reduced polarization of (*R,R*)-**3d** is essentially the same as that expected for an (*R*)-2-octyloxy side chain, which suggests that the average orientation of the (*R*)-fluorenol transverse dipole moment is approximately congruent with the smectic tilt plane, i.e., perpendicular to the polar axis, and that the core makes no significant contribution to the spontaneous polarization. These results are consistent with the expected rotational bias of the fluorenol core with respect to the side chains, which is imposed by the mean-field potential of the SmC* phase according to the Boulder model.²¹ Furthermore, the results indicate that the (*R*)- and (*S*)-fluorenol cores do not make equivalent contributions (in opposite directions along the polar axis) to the spontaneous polarization, which is consistent with steric coupling of the core to the chiral (*R*)-2-octyloxy side chain. We were unable to correlate these results to conformational analyses of (*R,R*)-**3d** and (*S,R*)-**3d** based on the assumptions of the Boulder model because of the complexity of their conformational distributions calculated at the AM1 level.

Conclusions

The synthesis of the new SmC* mesogens **2a–e** and **3a–e** reported herein is the first application of the combined DoM–DreM methodology in liquid crystal chemistry.^{30b} A comparison of phase transition temperatures for the fluorenone and fluorenol mesogens combined with variable-temperature IR measurements suggests that the SmC* phase formed by the fluorenol mesogens is stabilized by intermolecular hydrogen bonding between the hydroxy group and ester carbonyl group. Furthermore, a comparison of reduced polarization values for the two fluorenol diastereomers (*R,R*)-**3d** and (*S,R*)-**3d** suggests that the polar fluorenol core contributes to the spontaneous polarization of the latter. This is likely due to a rotational bias of the polar core with respect to the side chains imposed by the mean-field potential of the SmC* phase according to the Boulder model,²¹ and to steric coupling of the core to the chiral 2-octyloxy side chain. However, it is still unclear whether intermolecular hydrogen bonding also contributes to polar ordering of the fluorenol core as a form of cooperative effect. To address this question, the synthesis and characterization of SmC* mesogens with a chiral fluorenol core as the only stereopolar unit have been undertaken and will be reported in due course.

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Supporting Information Available: Full experimental details including synthetic procedures, full characterization of new compounds, physical measurement procedures, and a polarized photomicrograph of the SmX phase formed by compound **3b** in PDF format and X-ray crystallographic data including structure refinement parameters and tables of atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for compound (*R*)-**20** in CIF file format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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