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Chirality Transfer in
Ferroelectric Liquid Crystals

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ABSTRACT

This Account describes how concepts used in the fields of host-guest chemistry and chiral molecular recognition may be used to explain the unique chiral induction behavior of molecules with atropisomeric biphenyl cores when doped into a two-dimensionally ordered smectic liquid crystal phase formed by rod-shaped molecules with a phenylpyrimidine core structure.

Introduction

Liquid crystals were discovered more than a century ago and remained primarily the object of scientific curiosity until the discovery of the twisted nematic effect in 1971,¹ which launched the era of liquid crystal displays (LCD). The development of LCD panels has revolutionized the portable computer industry, and LCDs are now found in most electronic devices that require some form of information display. Yet, despite their ubiquitous nature, the unique properties of liquid crystals remain relatively unknown to scientists working outside the realm of materials science. A liquid crystal is an ordered fluid that is intermediate between the three-dimensionally ordered crystal phase and the disordered liquid phase; it is often referred to as a *mesophase* and its constituent molecules as *mesogens*. Materials that form a mesophase in the absence of solvent are *thermotropic* liquid crystals, and

phase transitions are observed as a function of temperature (Figure 1). Other materials that form a mesophase in the presence of a solvent, for example, lipids, soaps, and other surfactants, are *lyotropic* liquid crystals and will not be covered in this Account. The vast majority of thermotropic mesogens are rod-shaped compounds composed of a rigid aromatic core and alkyl side chains (*calamitic* liquid crystals); these materials can form two main classes of liquid crystal phases, the *nematic* and *smectic* phases.² Examples of calamitic liquid crystals used in the work described in this Account are shown in Figure 2.

The nematic phase (N) is a one-dimensionally ordered fluid in which molecular long axes are oriented along a vector \mathbf{n} (the *director*) but are otherwise completely disordered. In smectic phases, molecules are arranged in diffuse layers and show orientational and short-range positional order within the plane of the layers. Several smectic phases have been identified, but the two most commonly observed are the smectic A (SmA) and C (SmC) phases. In the SmA phase, molecular long axes are oriented along a director \mathbf{n} which is parallel to the layer normal \mathbf{z} ; in the SmC phase, the director \mathbf{n} is tilted at a temperature-dependent angle θ with respect to \mathbf{z} . Unlike the nematic phase, which completely lacks positional order, the diffuse layer structure of the SmA and SmC phases results, on the time average, in a segregation of the rigid cores from the side chains. This Account describes how such segregation may play a key role in amplifying the bulk properties of a chiral SmC phase.

By virtue of their fluid nature, liquid crystals are easily processed into thin films, yet they retain the optical properties of crystalline materials such as the ability to rotate plane-polarized light (*birefringence*). In addition, the orientation of polar molecules in liquid crystal films can be modulated on a relatively short time scale using a small electric field. Because the birefringence of a liquid crystal is a function of the angle formed by plane-polarized light and the director \mathbf{n} , a liquid crystal film can effectively function as an ON/OFF light shutter between crossed polarizers by electrically switching the liquid crystal film between two different molecular orientations relative to

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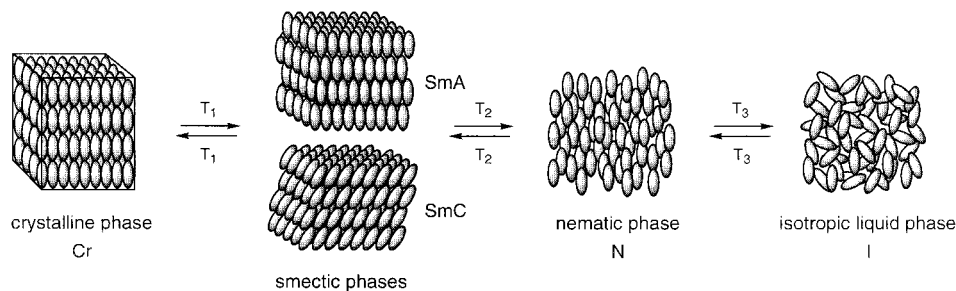
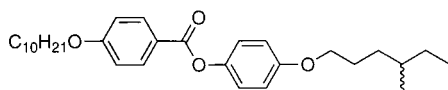
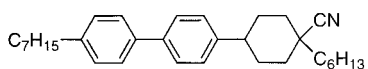


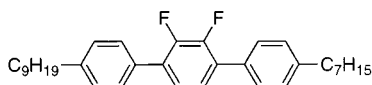
FIGURE 1. Phase transitions between crystal, liquid crystal, and isotropic liquid phases for a calamitic material as a function of temperature.



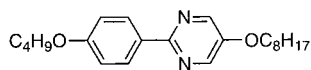
PhB; phase sequence: Cr 35 SmC 70.5 SmA 72 N 75 I



NCB76; phase sequence: Cr 66 (SmG 55) SmC 73 SmA 117 N 125 I



DFT; phase sequence: Cr 49 SmC 77 SmA 93 N 108 I



PhP1; phase sequence: Cr 58 SmC 85 SmA 95 N 98 I

FIGURE 2. Liquid crystal host structures and phase transition temperatures in °C.

the polarizers. Most liquid crystal applications are based on this simple concept of an ON/OFF light shutter. Although the vast majority of commercial LCDs use nematic liquid crystals, chiral SmC (SmC*) liquid crystals have received considerable attention as light shutters in the next generation of LCD devices, because they can be switched ON and OFF about 10^3 times faster than nematic liquid crystals.³⁻⁷

Under certain alignment conditions (vide infra), SmC* liquid crystals are ferroelectric; that is, they possess a macroscopic electric polarization that is oriented perpendicular to the smectic tilt plane (defined by the director \mathbf{n} and the layer normal \mathbf{z}). The origin of this electric polarization, known as *spontaneous polarization* (P_S), is first described at the macroscopic level by a simple symmetry argument⁸ and is later described at the molecular level using conformational analysis. On the time average, the symmetry elements of the achiral SmC phase include a C_2 axis normal to the tilt plane and a reflection plane of symmetry σ congruent to the tilt plane (Figure 3). If the SmC phase is chiral, it cannot possess reflection symmetry, and dipole moments along the C_2 axis are invariant with respect to the C_2 operation. The resulting electric polarization along the C_2 axis (*polar axis*) is a chiral bulk property intrinsic to each layer of the SmC* phase.

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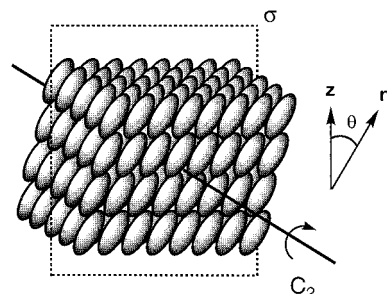


FIGURE 3. Schematic representation of the smectic C phase. The vectors \mathbf{z} and \mathbf{n} are congruent with the plane of the page, and the C_2 axis is normal to the plane of the page.

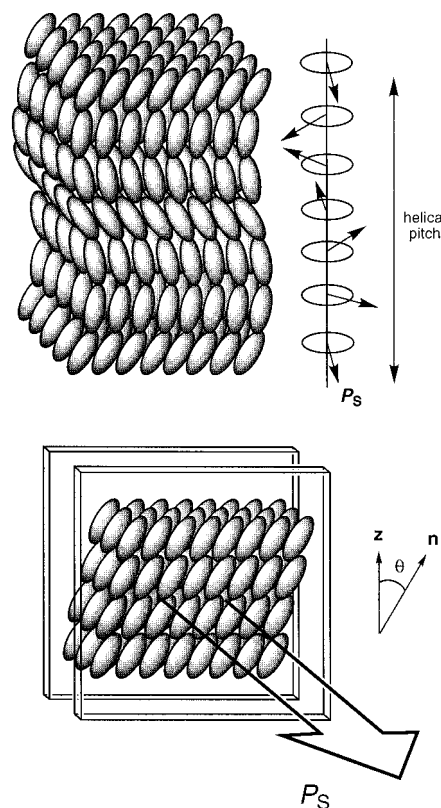


FIGURE 4. Schematic representation of the chiral smectic C* phase as a macroscopic helix in the absence of surface alignment (top) and as an SSFLC film between two glass slides (bottom).

However, in the absence of external constraints, the SmC* phase forms a macroscopic helical structure in which the P_S vector rotates from one layer to the next, thus averaging to zero in the bulk (Figure 4). This helical structure, with a pitch typically on the order of a few microns, is another chiral bulk property of the SmC* phase.

In 1980, Clark and Lagerwall showed that the helical SmC* phase spontaneously unwinds between polyimide-coated glass slides with a spacing on the order of the pitch to give a *surface-stabilized ferroelectric liquid crystal* (SSFLC) film with a net spontaneous polarization oriented perpendicular to the glass slides (Figure 4).⁹ By applying an electric field across the film, a SSFLC can be switched between two opposite tilt orientations (i.e., from $+\theta$ to $-\theta$) to give an ON/OFF light shutter between crossed polarizers. Commercial SmC* materials for SSFLC light shutter applications are normally obtained by mixing a chiral dopant with high polarization power (δ_p) into an achiral SmC liquid crystal mixture with low viscosity and wide temperature range. The polarization power is a measure of the propensity of a chiral dopant to induce a spontaneous polarization in a nonferroelectric SmC host according to eq 1, where x_d is the dopant mole fraction and P_o is the spontaneous polarization normalized for variations in tilt angle θ according to eq 2.^{10,11} Because the switching time achieved by SSFLC light shutters is inversely proportional to P_s ,⁴ the design of chiral dopants with increasingly high polarization powers has received considerable attention over the past 15 years.¹² To rationally design chiral dopants with high δ_p , a detailed understanding of the molecular origins of P_s is required.

$$\delta_p = \left(\frac{dP_o(x_d)}{dx_d} \right)_{x_d=0} \quad (1)$$

$$P_o = P_s / \sin \theta \quad (2)$$

Molecular Origins of the Spontaneous Polarization

In an induced SmC* phase, the transverse dipole moments of individual chiral dopant molecules contribute to the spontaneous polarization as a result of the ordering imposed by the SmC host. According to the Boulder model for the molecular origins of P_s , the ordering of dopant molecules in a SmC host can be modeled by a mean-field potential which qualitatively behaves like a binding site similar to that described in host–guest chemistry and biochemistry.^{13–15} The mean-field potential is approximately C_{2h} -symmetric and has a zigzag shape so that the molecular side chains are, on average, less tilted with respect to the smectic layer normal \mathbf{z} than is the molecular core (Figure 5).^{16,17} When a chiral dopant is confined to this “binding site”, steric coupling between a polar functional group and an adjacent stereocenter results in an orientational bias of the corresponding dipole moment along the polar C_2 axis that contributes to P_s (*polar ordering*). For example, a conformational analysis of the (*S*)-2-octyloxy side chain of a prototypical chiral dopant **1** confined to the SmC binding site (Figure 6) reveals that the polar alkoxy group can adopt one of two staggered conformations **A** and **B** in which the alkoxy dipole is oriented along the polar axis (the third staggered conformation orients the alkoxy dipole in the tilt plane and cannot contribute to P_s). These two conformations are nonequivalent, with conformation **A** being favored by the

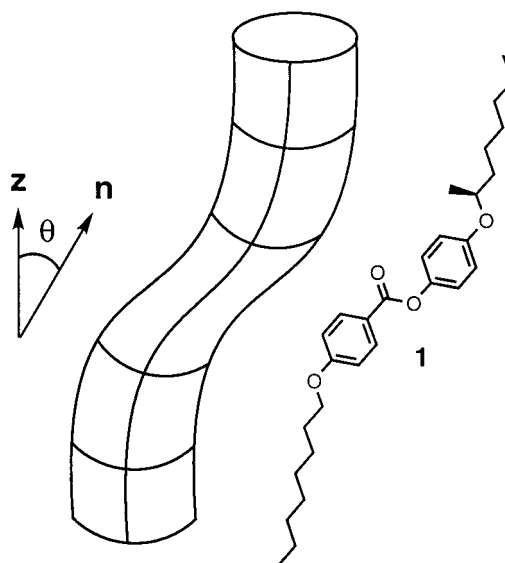


FIGURE 5. Zigzag binding site according to the Boulder model.

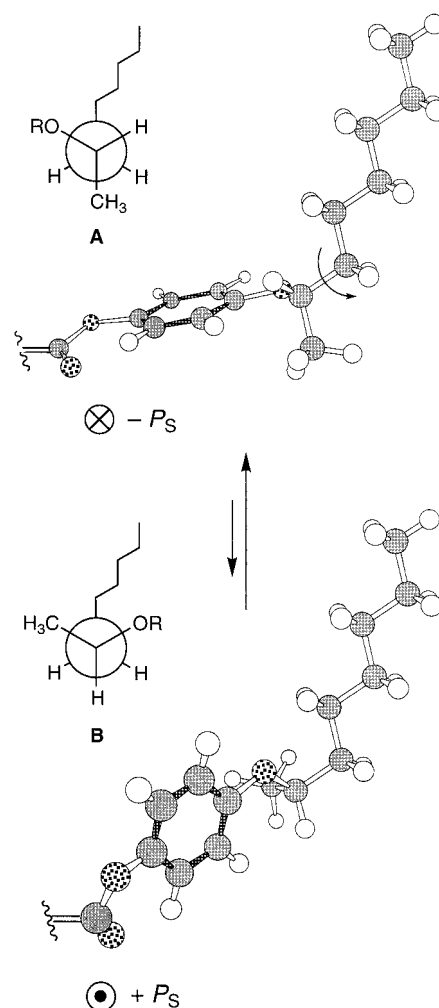


FIGURE 6. Conformations of the 2-octyloxy side chain of dopant **1** confined to the binding site as AM1-minimized models and as Newman projections about the C2–C3 bond.

anti relationship between the methyl group and the C4 methylene group, thus resulting in a negative P_s . Hence, the magnitude and sign of P_s are a function of the energy

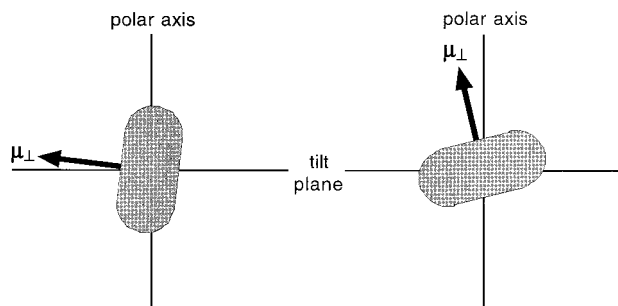


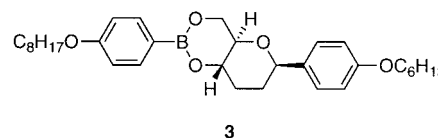
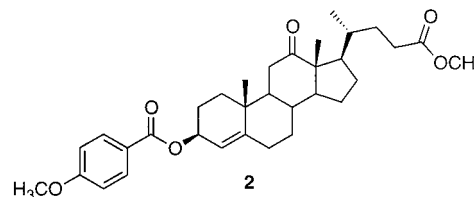
FIGURE 7. Two different rotational distributions of a Type II chiral dopant and its transverse dipole moment μ_{\perp} viewed along the molecular long axis.

difference between conformations **A** and **B** (*conformational asymmetry*).

An analysis of the molecular origins of P_S must invariably focus on the structural unit containing the stereocenter and any polar functional group sterically coupled to the stereocenter (the so-called *stereo-polar unit*). The vast majority of chiral dopants known to induce a SmC* phase have stereo-polar units (SPU) located in one of the side chains (e.g., **1**) and have polarization powers that are relatively independent of the structure of the achiral SmC host (Type I).¹⁸ This behavior reflects a lack of molecular recognition by the SPU, because of the high degree of conformational disorder in the side chain region of the SmC layer, and is consistent with a basic approximation of the Boulder model that the shape of the binding site is invariant with respect to the host structure. On the other hand, chiral dopants with SPUs located in the rigid core (e.g., **2** and **3**) generally have polarization powers that vary with the structure of the host (Type II). This host effect can be viewed as a manifestation of molecular recognition by the SPU through core-core interactions with surrounding SmC host molecules and reflects a higher conformational rigidity in the core region of the SmC layer.

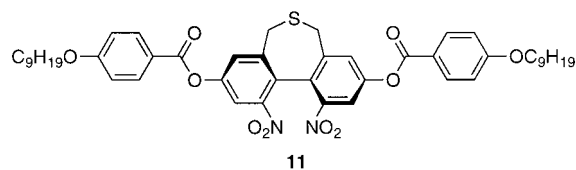
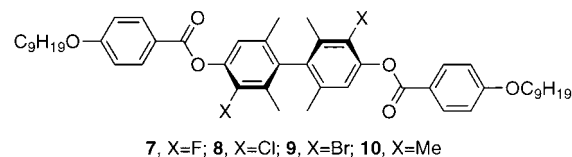
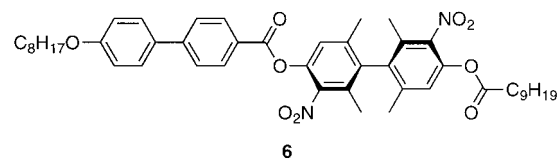
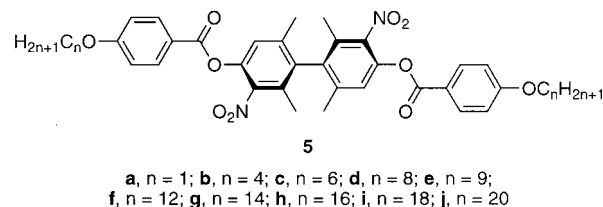
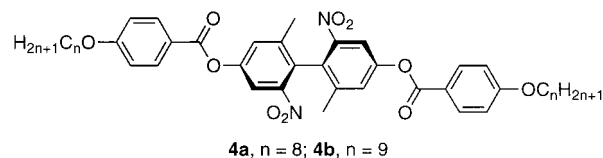
Stegemeyer explained the Type II host effect using a mathematical description of P_S that includes two terms: (i) a *polar ordering* term that is a function of the conformational asymmetry of the SPU (*vide supra*) and (ii) a *rotational distribution* term that describes the orientation of the SPU transverse dipole moment (μ_{\perp}) with respect to the polar axis.¹⁸ According to this model, the Type II host effect arises primarily from variations in rotational distribution of μ_{\perp} caused by rigid core-core interactions with surrounding host molecules. Hence, a Type II dopant with high polar ordering may induce a low P_S in one host if μ_{\perp} is oriented near the tilt plane and a high P_S in another host if μ_{\perp} is oriented near the polar axis (Figure 7). This explanation may be reconciled with the Boulder model by assuming that the central part of the binding site changes shape from one host to the next. As a first approximation, the dopant is assumed to play the role of a *passive* guest which must adopt a particular conformation and orientation that best "fit" the binding site of the SmC host. This approximation is certainly reasonable in the case of Type I dopants. However, the research described in this Account suggests that, in some cases, a Type II dopant may play the role of an *active* guest that

modifies the topography of the binding site by intermolecular chirality transfer. This research focuses on a new class of Type II chiral dopants with atropisomeric biphenyl cores which are designed to induce high spontaneous polarizations.



Dopants with Atropisomeric Biphenyl Cores

Dinitro Series. The first example of a chiral dopant with an atropisomeric biphenyl core reported to induce a ferroelectric SmC* phase is the 2,2'-dinitro dopant **4a**.^{19,20} The spontaneous polarization induced by **4a** is thought to originate from a small bias in the energy profile for rotation of the rigid biphenyl core about the two ester



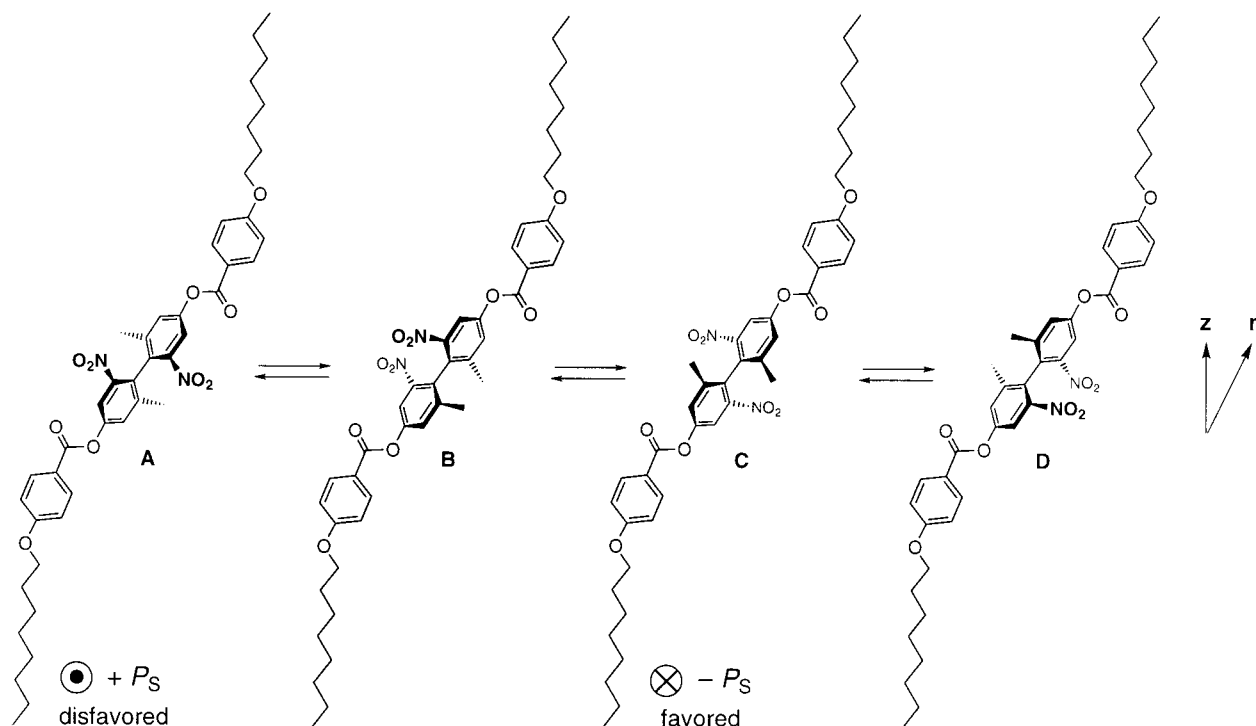


FIGURE 8. Rotation of the atropisomeric biphenyl core about the two ester C–O bonds in dopant **4a** with the molecule in an AM1-minimized zigzag conformation. The tilt plane is in the plane of the page.

C–O bonds. Using the idealized zigzag conformation shown in Figure 8, calculations predict that a 360° rotation of the biphenyl core gives four energy minima which correspond approximately to structures A–D.²⁰ Of these four rotamers, only A and C have a transverse dipole moment along the polar axis which contributes to P_S ; the transverse dipole moments of rotamers B and D lie in the tilt plane and cannot contribute to P_S . These calculations predict that rotamer C, in which the carbonyl groups are quasi *anti*-periplanar with respect to the nitro groups, is favored over the corresponding quasi *syn*-periplanar rotamer A by ~ 0.2 kcal/mol.

Conformational analyses on other model systems have shown that the rotational energy bias of the atropisomeric biphenyl core as modeled in Figure 8 should be significantly larger when the symmetry-breaking group (e.g., NO_2) is positioned *ortho* to the benzoate group.^{21,22} To test the validity of such analyses in predicting relative values of δ_p for dopants with atropisomeric biphenyl cores, a series of 3,3'-dinitro dopants **5a–j** and **6**, and other 3,3'-disubstituted dopants **7–10** were investigated in four different SmC liquid crystal hosts (Figure 2).^{21–24} The polarization power data obtained for dopants **4a** and **5a–j** revealed some important trends. First, δ_p values for the 2,2'-dinitro dopant **4a** are significantly smaller than those for the corresponding 3,3'-dinitro dopant **5d** (Figure 9), which is consistent with the rotational bias calculations. Second, the polarization power of all dopants strongly depends on the nature of the SmC host, as predicted by Stegemeyer for a Type II dopant, but on a much larger scale than reported heretofore (Figure 10). Remarkably, the polarization power of **5d** in **PhP1** (1738 nC/cm^2) is one of the highest reported thus far in the literature for a

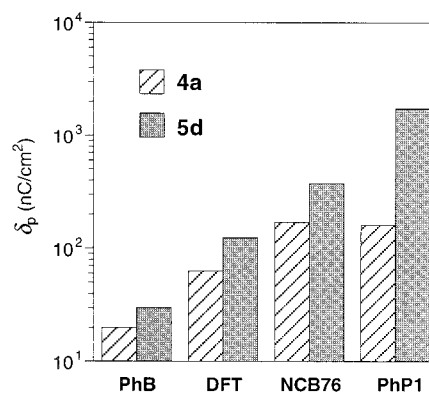


FIGURE 9. Polarization power δ_p of dopants **4a** and **5d** in the SmC hosts **PhB**, **DFT**, **NCB76**, and **PhP1** measured at 5 K below the $\text{SmC}^*-\text{SmA}^*$ phase transition temperature ($T-T_C = -5 \text{ K}$).

chiral dopant of any type. Third, the polarization power of dopants **5a–j** varies with the length of the alkoxy side chains n (Figure 10). Because longer alkyl chains are expected to increase the positional ordering (e.g., core–core correlation) of the dopant with respect to surrounding host molecules, these results suggest that δ_p is enhanced by core–core interactions between dopant and host molecules.

According to Figure 10, the dependence of δ_p on core–core interactions appears to be particularly important, indeed unique, in the phenylpyrimidine host **PhP1**. To further assess the influence of core–core interactions on δ_p , we designed the asymmetrical dopant **6**, which has approximately the same length as the symmetrical dopant **5d**. In this configuration, the position of the atropisomeric core is shifted away from the core sublayer of the SmC host, thus reducing core–core interactions with surround-

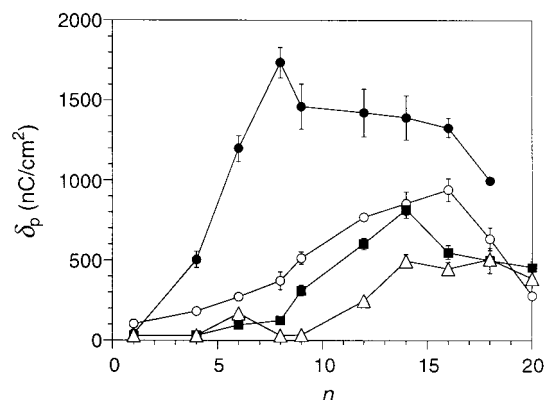


FIGURE 10. Polarization power δ_p versus alkoxy chain length n for dopants **5a–j** in the SmC hosts **PhB** (triangles), **DFT** (squares), **NCB76** (open circles), and **PhP1** (filled circles) at $T-T_c = -5$ K.

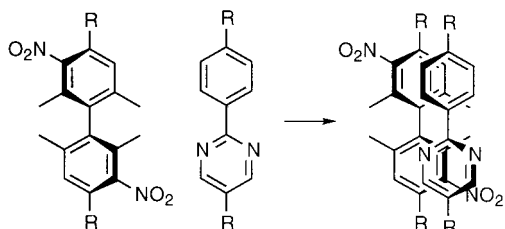


FIGURE 11. Model for core–core chirality transfer via chiral conformational interactions.

ing host molecules on the time average. As expected, we found that the polarization power of **6** in **PhP1** is $\sim 35\%$ less than that of **5d** (1101 nC/cm^2 vs 1738 nC/cm^2 , respectively).

To elucidate the molecular origins of this pronounced Type II behavior, we sought to understand the nature of core–core interactions between the dopant and SmC host molecules and how they influence the polarization power. In the ground state, the core structures of most SmC mesogens assume either an axially chiral conformation that rapidly interconverts between enantiomeric forms (e.g., **PhB**, **DFT**, **NCB76**), or a planar conformation that can be distorted into an axially chiral form (e.g., **PhP1**). Given the orientational ordering imposed by the SmC phase, core–core interactions between an atropisomeric biphenyl dopant and neighboring host molecules should result in a chiral perturbation of the host phase (i.e., *chirality transfer*). Such perturbation may take the form of a nonracemic mixture of axially chiral conformers or that of axially distorted chiral core structures. According to an empirical model first proposed by Gottarelli et al. for chiral induction in nematic liquid crystals, such chirality transfer is likely to take place via chiral conformational interactions (Figure 11), which require a good structural match to be effective.²⁵ In the cases described in this Account, the best structural match for chirality transfer via core–core interactions is the phenylpyrimidine core of **PhP1**, while the worst structural match is the phenyl benzoate core of **PhB**, in which the smallest polarization powers are obtained.

The degree of chirality transfer from a dopant to SmC host molecules may be correlated to the inverse helical pitch $1/p$ of the induced SmC* phase (Figure 4) when

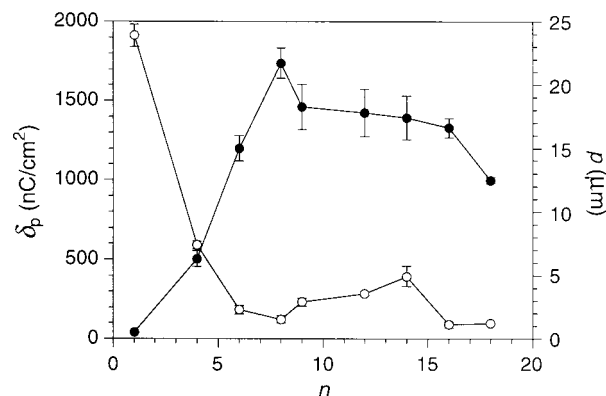


FIGURE 12. Polarization power δ_p (filled circles) and SmC* helical pitch p (open circles) versus alkoxy chain length n for dopants **5a–i** in the SmC host **PhP1**.

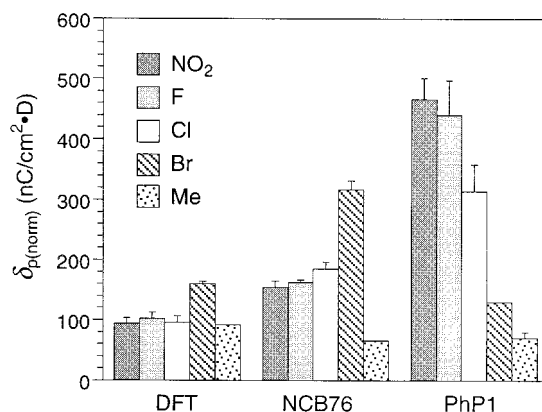


FIGURE 13. Normalized polarization power $\delta_{p(\text{norm})}$ for dopants **5e** and **7–10** in the SmC hosts **DFT**, **NCB76**, and **PhP1** at $T-T_c = -5$ K. The $\delta_{p(\text{norm})}$ values for dopant **10** ($X = \text{Me}$) in **DFT** and **NCB76** are estimated upper limits.

external constraints such as surface stabilization are absent. In the host **PhP1**, we found that the pitch of the SmC* phase induced by dopants **5a–j** ($x_d = 0.02$) varies with the chain length n and follows a trend opposite to that observed for δ_p versus n (Figure 12). This result proved to be the first clue suggesting that chirality transfer via core–core interactions may play an important role in enhancing the polarization power of atropisomeric biphenyl dopants.

Influence of the Symmetry-Breaking Groups on δ_p .

In a more recent study, we focused our attention on the influence of the symmetry-breaking groups on δ_p in the dopant series **5e** and **7–10** ($X = \text{NO}_2$, F, Cl, Br, and Me).^{22,24} The polarization power depends strongly on the nature of the symmetry-breaking groups, which is due in part to differences in the core transverse dipole moment μ_{\perp} contributing to the induced polarization. To study the influence of X in terms of core–core interactions with the SmC host, δ_p values were normalized for differences in μ_{\perp} based on ab initio calculations at the B3LYP/6-31G(d) level.²² As shown in Figure 13, the normalized polarization power $\delta_{p(\text{norm})}$ strongly depends on the nature of the SmC host (the induced P_S in **PhB** was too small to be measured), and the trend followed by $\delta_{p(\text{norm})}$ as a function of X in **PhP1** is clearly distinct from that observed in **DFT** and **NCB76**. Interestingly, $\delta_{p(\text{norm})}$ correlates with the

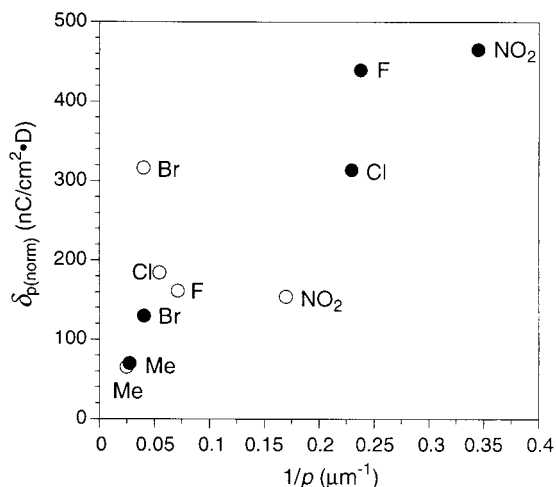


FIGURE 14. Normalized polarization power $\delta_p(\text{norm})$ versus inverse SmC* helical pitch $1/p$ for dopants **5e** and **7–10** in the SmC hosts **PhP1** (filled circles) and **NCB76** (open circles). The $1/p$ value for dopant **10** (X=Me) in **NCB76** is an estimated upper limit.

inverse helical pitch $1/p$ in **PhP1** but not in **NCB76** (Figure 14), which is consistent with the previous observations and suggests that chirality transfer via core–core interactions plays a unique role in enhancing δ_p in the host **PhP1**.

Influence of Helical Topography on δ_p . Chiral induction in cyanobiphenyl nematic liquid crystals is known to be more effective using a bridged biaryl dopant with helical topography rather than the corresponding unbridged compound.^{25–28} This structure–property relationship is consistent with the chirality transfer model of Gottarelli et al. and provides another opportunity to assess the influence of core–core chirality transfer on δ_p . Hence, we synthesized the bridged biphenyl dopant **11** and compared it to the unbridged dopant **4b** in terms of polarization power and induced SmC* pitch p measured at $x_d = 0.02$.^{19,29} As in previous cases, the data show an inverse relationship between δ_p and p , which supports the idea that chirality transfer enhances δ_p . After normalizing for differences in core transverse dipole moment, we found that $\delta_p(\mathbf{11})$ is greater than $\delta_p(\mathbf{4b})$ (99.1 $\text{nC}/\text{cm}^2\text{-D}$ vs 18.8 $\text{nC}/\text{cm}^2\text{-D}$, respectively) while $p(\mathbf{11})$ is shorter than $p(\mathbf{4b})$ (14.2 μm vs 95.8 μm , respectively).

Probe Experiments

To obtain a more direct assessment of the chiral perturbation exerted by an atropisomeric dopant on surrounding host molecules (i.e., on the binding site), we studied the effect of dopant **5e** on the polarization induced by a second chiral dopant (*probe*) which mimics the structure of the SmC host.³⁰ The Displaytech compound **MDW950** and the phenyl benzoate **12** were used as probes in the SmC hosts **PhP1** and **PhB**, respectively. In the first part of the “probe” experiment, a reference plot is obtained by measuring the normalized polarization P_o (eq 2) of SmC* mixtures composed of the probe and SmC host over the mole fraction range $0 \leq x_{\text{probe}} \leq 0.30$. In the second part of the experiment, the P_o measurements are repeated in the presence of the atropisomeric dopant at a constant mole fraction $x_d = 0.04$. The resulting plot of P_o versus

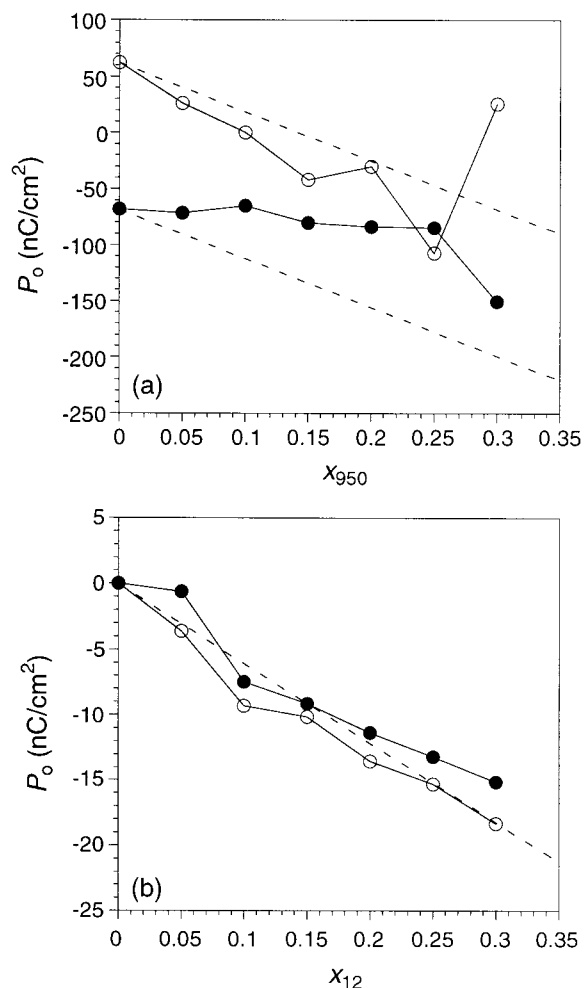
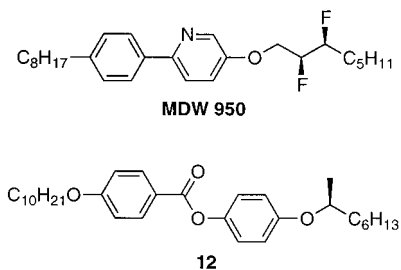


FIGURE 15. (a) Normalized polarization P_o versus mole fraction of **MDW950** x_{950} in the presence of (+)-**5e** (open circles) and (–)-**5e** (filled circles) at a constant mole fraction $x_d = 0.04$ in the SmC host **PhP1** at $T - T_c = -5$ K. The dashed lines correspond to the least-squares fit from the reference plot shifted by P_o at $x_{950} = 0$. (b) Normalized polarization P_o versus mole fraction of **12** x_{12} in the presence of (+)-**5e** (open circles) and (–)-**5e** (filled circles) at a constant mole fraction $x_d = 0.04$ in the SmC host **PhB** at $T - T_c = -5$ K.

x_{probe} is compared to the reference plot, which is shifted along the y-axis by a value equal to P_o induced by the atropisomeric dopant in the absence of the probe (Figure 15). In each case, the shifted reference plot represents the result expected if the polarizations induced by the atropisomeric dopant and the probe are simply additive, that is, if the dopant is passive and does not perturb the probe/host mixture. On the other hand, if the atropisomeric dopant is active and perturbs the probe/host mixture, a variation in the polarization induced by the probe should be observed because of the effect of the perturbation on the polar ordering and/or rotational distribution of the probe (vide supra). Experimentally, such a variation in P_o will cause the P_o versus x_{probe} plot to deviate from the reference plot. Whether the perturbation exerted by the atropisomeric dopant is chiral or achiral in nature can be determined by comparison of the plots obtained with each enantiomeric form of the atropisomeric dopant. If the perturbation is achiral in nature, the two plots should be

superposable; if the perturbation is chiral in nature (i.e., chirality transfer), the two plots should not be superposable, because the two enantiomers of the atropisomeric dopant form diastereomeric pairs with the chiral probe molecule.



The P_o versus x_{probe} plots obtained in the probe experiments are approximately linear up to $x_{\text{probe}} = 0.25$; the deviations from linearity observed in **PhP1** at $x_{950} = 0.30$ may be due to a cooperative effect that partially counters the perturbation of the atropisomeric dopant. If one ignores the two data points at $x_{950} = 0.30$, the results in Figure 15a show that the polarization power of **MDW950** increases in the presence of (+)-**5e**, but decreases in the presence of the other enantiomer, (–)-**5e**. This result suggests that **5e** exerts a significant chiral perturbation on the phenylpyrimidine host. On the other hand, the results in Figure 15b suggest that **5e** does not perturb the phenyl benzoate host to any significant extent and simply behaves as a passive guest.

Chirality Transfer Feedback Model

The results summarized in this Account suggest that the spontaneous polarization induced by an atropisomeric biphenyl dopant is enhanced by a chiral perturbation of the SmC host matrix through core–core interactions. Such chiral perturbation appears to be particularly strong in the SmC host **PhP1** by virtue of the favorable structural match between the phenylpyrimidine core of **PhP1** and the atropisomeric biphenyl core of the chiral dopant. But one question remains: How does chirality transfer influence the induced spontaneous polarization?

Stegemeyer proposed that intermolecular chirality transfer can contribute to the Type II host effect by causing a polar ordering of the SmC host.¹⁸ In this scenario, the perturbed SmC host molecules effectively become chiral dopants and induce an additional spontaneous polarization that should scale with the core transverse dipole moment of the host molecule. However, in comparison to the other SmC hosts, the phenylpyrimidine core of **PhP1** is unlikely to contribute to P_S as a result of chirality transfer. We recently proposed a different mechanism in which chirality transfer results in a chiral distortion of the binding site (Figure 16).²¹ As a feedback, this chiral distortion can increase the polar ordering of the dopant by causing a shift in the conformational equilibrium of the atropisomeric core with respect to the ester side chains (Figure 8). This shift in conformational equilibrium occurs by virtue of the diastereomeric rela-

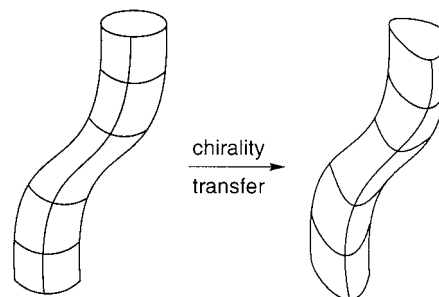


FIGURE 16. Chiral distortion of the SmC binding site.

tionship between “host–guest complexes” formed by the various chiral conformers of the dopant and the chiral binding site. The chiral distortion can also increase P_S by causing a shift in the rotational distribution of the core transverse dipole moment μ_{\perp} toward the polar axis (Figure 7).

The proposed *chirality transfer feedback* (CTF) model assumes that a chiral dopant behaves as an active guest which perturbs the topography the binding site. It differs from classical host–guest chemistry or chiral molecular recognition analogies in the sense that chiral perturbation of the host matrix has a feedback effect on the dopant itself and may therefore be viewed as a form of *dynamic* chiral molecular imprinting.³¹ By contrast, the Boulder model assumes that the chiral dopant behaves as a passive guest in a binding site that is approximately C_{2h} -symmetric. It is important to note that these two models are not mutually exclusive and that the Type II host effect may be due to differences in the intrinsic topography of the SmC binding site as well as in the degree of chiral distortion of the binding site. Indeed, the CTF model may be viewed conceptually as an extension of the Boulder model that accounts for the unique behavior of a new class of chiral dopants. The studies described in this Account suggest that the relative contribution of each effect is a function of the propensity of a Type II dopant to transfer chirality to the SmC host via core–core interactions.

Summary

The spontaneous polarization induced by chiral dopants with atropisomeric biphenyl cores depends strongly on the core structure of the SmC liquid crystal host. Such dependence can be explained using the Boulder model on the basis of the assumption that a chiral dopant is ordered in the SmC phase by a mean-field potential analogous to a binding site. In one scenario, the atropisomeric dopant behaves as a passive guest and responds to changes in the intrinsic topography of the achiral binding site. In another scenario, the atropisomeric dopant behaves as an active guest and perturbs the binding site through core–core interactions with surrounding host molecules. Such interactions are assumed to be chiral in nature, thus resulting in a chiral distortion of the binding site topography which leads to a feedback response by the chiral dopant. In either scenario, the dopant “response” may take the form of a shift in

rotational distribution of the transverse dipole moment and/or a change in polar ordering of the stereo-polar unit. The work described in this Account suggests that the chirality transfer feedback mechanism may predominate in cases where there is a favorable structural match between dopant and host molecules to undergo chirality transfer via core-core interactions and that rational design of chiral dopants with very high polarization powers may be achieved by careful mixing and matching of dopant and host core structures.

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