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Detection of Chiral Perturbations in Ferroelectric Liquid Crystals Induced by an Atropisomeric Biphenyl Dopant

C. Scott Hartley,[†] Carmen Lazar,[†] Michael D. Wand,[‡] and Robert P. Lemieux*,[†]

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6, and Displaytech, Inc., 2602 Clover Basin Drive, Longmont, Colorado 80503

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Abstract: The atropisomeric dopant 2,2′,6,6′-tetramethyl-3,3′-dinitro-4,4′-bis[(4-nonyloxybenzoyl)oxy]biphenyl (**1**) induces a ferroelectric SmC* phase when doped into the SmC liquid crystal hosts 2-(4-butyloxyphenyl)-5-octyloxypyrimidine (**PhP1**) and (±)-4-[(4-methylhexyl)oxy]phenyl 4-decyloxybenzoate (**PhB**). The propensity of dopant **1** to induce a spontaneous polarization (polarization power) is much higher in **PhP1** than in **PhB** (1555 nC/cm^2 vs <35 nC/cm^2), which is attributed to a greater propensity of **1** to undergo chirality transfer via core−core interactions with **PhP1**. In previous work, we postulated that a chiral perturbation exerted by **1** in **PhP1** amplifies the polarization power of the dopant by causing a chiral distortion of the mean field potential (binding site) constraining the dopant in the SmC host, as described by the Chirality Transfer Feedback (CTF) model. To test the validity of the CTF model, and to provide a more direct assessment of the chiral perturbation exerted by dopant **1** on surrounding host molecules, we measured the effect of **1** on the polarization power of other chiral dopants acting as probes. In one series of experiments, (*S,S*)-5-(2,3-difluorooctyl)-2-(4-octylphenyl)pyridine (**MDW950**) and (*S*)-4-(1-methylheptyloxy)phenyl 4-decyloxybenzoate (**4**), which mimic the structures of **PhP1** and **PhB**, were used as probes. In another series of experiments, the atropisomeric dopant 2,2′,3,3′,6,6′-hexamethyl-4,4′-bis[(4-nonyloxybenzoyl)oxy]biphenyl (**2**) was used as probe in **PhP1**. The results of the probe experiments suggest that dopant **1** exerts a much stronger chiral perturbation in **PhP1** than in **PhB**. More significantly, the results of experiments using **2** as probe show that the chiral perturbation exerted by **1** can amplify the polarization power of another atropisomeric dopant, thus providing the first experimental evidence of the CTF effect.

Introduction

Rod-shaped organic molecules formed by a rigid aromatic core and two paraffinic side-chains tend to exhibit a rich mesomorphism that includes one or more smectic liquid crystal phase(s).[1] The two most commonly observed smectic phases are the smectic A (SmA) and C (SmC) phases, in which molecules are arranged in diffuse layers and show orientational and short-range positional order within the plane of the layers. Over the past two decades, chiral smectic liquid crystals, including the ferroelectric SmC*, antiferroelectric SmC$_a$*, and electroclinic SmA* phases, have emerged as electrooptical materials of choice for the next generation of display applications.[2] Ferroelectric SmC* liquid crystals (FLC) hold tremendous potential in high-resolution reflective microdisplays due to their fast electrooptical switching time and bistability; these devices are currently used as color viewfinders in digital cameras and camcorders.[3,4] In a surface-stabilized planar alignment, SmC* liquid crystals exhibit a macroscopic electric polarization—the spontaneous polarization (P_S)—which is oriented perpendicular to a tilt plane defined by the molecular director **n** and the layer normal **z** and coincides with the C_2 symmetry axis (polar axis) of the SmC* phase (Figure 1). The spontaneous polarization is a macroscopic manifestation of molecular chirality. It originates from a conformational preference of transverse molecular dipoles to orient in one direction along the polar axis due to steric coupling of polar functional groups to one or more stereocenter(s) in the chiral molecules forming the SmC* phase.[5]

By virtue of the spontaneous polarization, a surface-stabilized FLC can be driven between two tilt orientations (i.e., from a tilt angle $+\theta$ to $-\theta$) by applying an electric field across the film to give an ON/OFF light shutter between crossed polarizers.[6] The spontaneous polarization is a key parameter in FLC microdisplays because the electrooptical ON/OFF switching time is inversely proportional to P_S.[3] In commercial SmC* mixtures, the spontaneous polarization is normally induced by mixing

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[†] Queen's University.

[‡] Displaytech, Inc.

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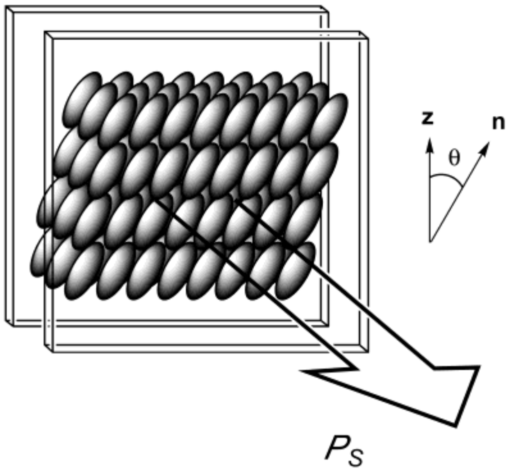


Figure 1. Schematic representation of the chiral smectic C^* phase as a surface-stabilized FLC film between two glass slides. The vectors **z** and **n** are in the plane of the page and form a tilt angle θ. The polar axis is coincident with the P_S vector and is normal to the plane of the page.

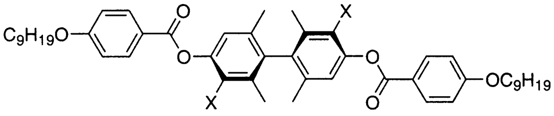
small amounts of a chiral dopant with a mixture of achiral SmC liquid crystals. This approach makes possible the optimization of nonchiral parameters such as viscosity and mesophase temperature range by formulating mixtures of relatively inexpensive achiral liquid crystal components. To minimize the amount of chiral material introduced in SmC* formulations, chiral dopants with high polarization powers (δ_p) have been sought.[7] The polarization power is a measure of the propensity of a chiral dopant to induce a spontaneous polarization according to eq 1, where x_d is the dopant mole fraction and P_o is the reduced polarization normalized for variations in tilt angle θ according to eq 2[8,9]

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

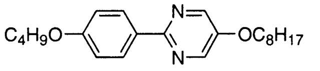
$$P_o = P_S / \sin\theta \tag{2}$$

The design of chiral dopants with high polarization powers must invariably focus on the structural unit containing the stereocenter and the polar functional group(s) sterically coupled to the stereocenter (the so-called *stereo-polar unit*). The vast majority of chiral dopants found in SmC* formulations have stereo-polar units located in one of the side-chains and, in general, the polarization power of these compounds is invariant with respect to the SmC host structure. This behavior is consistent with the Boulder model for the molecular origins of P_S.[5,10] According to this model, the conformational and orientational ordering imposed on a dopant molecule by the 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. The mean field potential is approximately C_{2h}-symmetric and has a zigzag shape that is assumed to be invariant with respect to the SmC host structure. As a first approximation, the Boulder model assumes that a chiral dopant plays the role of a "passive" guest which adopts a particular conformation that best fits the achiral binding site of the SmC host.

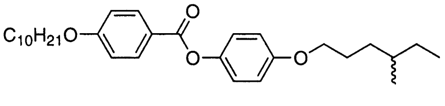
In certain cases, the structure of the SmC host must be taken into consideration. Unlike conventional dopants with chiral side-chains, dopants with stereo-polar units located in the rigid aromatic core tend to exhibit polarization powers that vary significantly with the structure of the SmC host.[11,12] This so-called Type II host effect may be viewed as a manifestation of molecular recognition via core−core interactions with surrounding host molecules which cannot be achieved with conventional dopants due to the higher degree of conformational disorder among side-chains in the diffuse layer structure of the SmC phase. In other words, the assumption that the shape of the binding site is invariant with the SmC host structure appears to break down in the case of dopants with chiral cores. For example, we have shown that the polarization power of chiral dopants with atropisomeric biphenyl cores (e.g., **1**) depends very strongly on the core structure of the SmC host.[12] Some of these dopants exhibit remarkably high polarization powers—as high as 1738 $\mathrm{nC/cm^2}$—in the phenylpyrimidine host **PhP1**.[13] On the other hand, the same dopants exhibit polarization powers of less than 35 $\mathrm{nC/cm^2}$ in the phenyl benzoate host **PhB**.



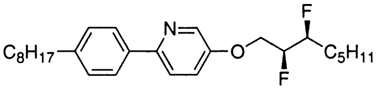
1, X=NO$_2$; **2**, X=Me; **3**, X=Cl



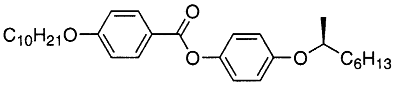
PhP1; phase sequence: Cr 58 SmC 85 SmA 95 N 98 I



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



MDW 950



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In the host **PhP1**, we have found that δ_p is uniquely sensitive to the positional ordering of the atropisomeric core with respect

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(7) For examples of chiral dopants with high polarization powers, see: (a) Ikemoto, T.; Sakashita, K.; Kageyama, Y.; Terada, F.; Nakaoka, Y.; Ichimura, K.; Mori, K. *Chem. Lett.* **1992**, 567. (b) Dübal, H. R.; Escher, C.; Günther, D.; Hemmerling, W.; Inogushi, Y.; Müller, I.; Murakami, M.; Ohlendorf, D.; Wingen, R. *Jpn. J. Appl. Phys.* **1988**, *27*, L2241. (c) Nishide, K.; Nakayama, A.; Kusumoto, T.; Hiyama, T.; Takehara, S.; Shoji, T.; Osawa, M.; Kuriyama, T.; Nakamura, K.; Fujisawa, T. *Chem. Lett.* **1990**, 623. (d) Kusumoto, T.; Sato, K.; Ogino, K.; Hiyama, T.; Takehara, S.; Osawa, M.; Nakamura, K. *Liq. Cryst.* **1993**, *14*, 727. (e) Sakashita, K.; Ikemoto, T.; Nakaoka, Y.; Terada, F.; Sako, Y.; Kageyama, Y.; Mori, K. *Liq. Cryst.* **1993**, *13*, 71. (f) Kobayashi, S.; Ishibashi, S.; Takahashi, K.; Tsuru, S.; Yamamoto, F. *Adv. Mater.* **1993**, *5*, 167. (g) Ikemoto, T.; Kageyama, Y.; Onuma, F.; Shibuya, Y.; Ichimura, K.; Sakashita, K.; Mori, K. *Liq. Cryst.* **1994**, *17*, 729.

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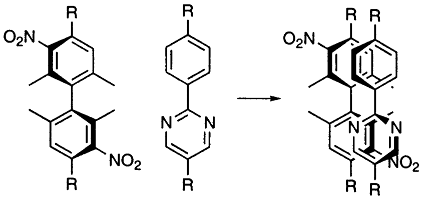

Figure 2. Model for core−core chirality transfer via chiral conformational interactions.

to the core sublayer of the SmC phase and that δ_p correlates to the inverse pitch $1/p$ of the helical structure formed by the induced SmC* phase in the absence of surface-stabilization.[14−16] These results suggest that, unlike conventional dopants with chiral side-chains, atropisomeric biphenyl dopants such as **1** do not behave as passive guests in the SmC liquid crystal host. Instead, these chiral dopants appear to behave as "active" guests which cause a chiral perturbation of the SmC liquid crystal host. In **PhP1**, this chiral perturbation is most likely achieved by inducing homochiral core conformations (i.e., chirality transfer) in surrounding host molecules via core−core conformational interactions, as described in Figure 2.[17] This empirical model was first proposed by Gottarelli and co-workers for the induction of chiral nematic (cholesteric) phases to account for the unusually high helical twisting power of atropisomeric biaryl dopants in nematic liquid crystals with complementary core structures such as 4-cyano-4′-pentylbiphenyl (5CB).[18,19] More recent work has also shown that atropisomeric biaryl dopants behave as active guests in solutions of poly(*n*-hexylisocyanate) by causing an excess of one helical sense of the dynamically racemic helical polymer, which results in the induction of a lyotropic cholesteric phase.[20] The effect of chiral conformational interactions between an atropisomeric biaryl dopant and biphenyl solvents has even been observed, albeit to a lesser extent, in isotropic solution by optical rotatory power measurements.[21]

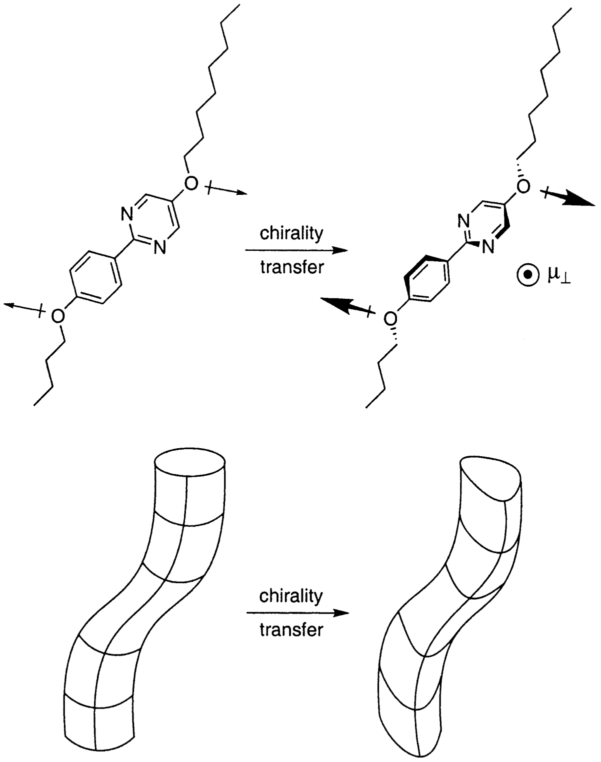

Figure 3. Two possible effects of chirality transfer: polar ordering of the SmC host (top), and chiral distortion of the SmC binding site (bottom). In each case, the polar axis is normal to the plane of the page.

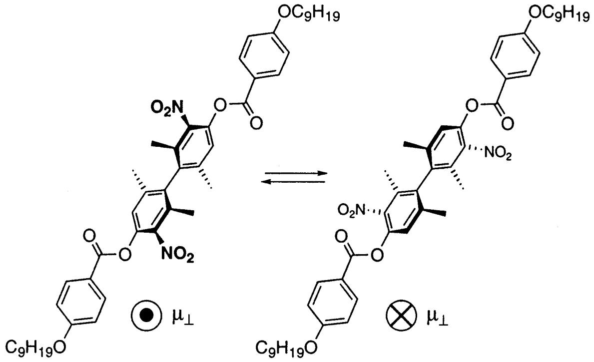

Figure 4. Rotation of the atropisomeric core about the two ester C−O single bonds of dopant **1** confined to the SmC binding site in an idealized zigzag conformation. The polar axis is normal to the plane of the page and the direction of the core transverse dipole moment $\mu_\perp$ is shown for each conformation.

Despite the accumulating experimental evidence suggesting a link between chirality transfer and the high δ_p values of atropisomeric biphenyl dopants in **PhP1**, the mechanism by which chirality transfer amplifies the spontaneous polarization remains in question. Stegemeyer first proposed that chirality transfer could amplify the spontaneous polarization by causing a polar ordering of the SmC host.[11] According to this model, the perturbed host molecules effectively become chiral dopants and produce an additional polarization that scales with the core transverse dipole moment ($\mu_\perp$) of the host molecules. In the present case, a chiral perturbation of the planar dialkoxyphenylpyrimidine core could produce a chiral conformation in which the two alkoxy dipoles contribute to P_S (Figure 3, top).[17] Recently, we proposed that chirality transfer could also have a feedback effect on the polarization power of the chiral dopant.[14] The spontaneous polarization induced by dopants such as **1** is thought to originate from a small bias in the energy profile for rotation of the biphenyl core about the two ester C−O single bonds which results in a preferred orientation of the core transverse dipole moment along the polar axis (Figure 4). According to the Chirality Transfer Feedback (CTF) model, a chiral perturbation of surrounding host molecules causes a chiral distortion of the binding site which, as a feedback, causes a

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shift in the conformational equilibrium of the dopant favoring one orientation of $\mu_\perp$ along the polar axis (Figure 3, bottom). The shift occurs by virtue of the diastereomeric relationship between "host-guest complexes" formed by the various chiral conformers of the dopant and the chiral binding site. A chiral distortion of the binding site could also result in a higher spontaneous polarization by causing a shift in the net orientation of $\mu_\perp$ with respect to the polar axis (rotational distribution).[11]

Thus far, experimental evidence for a chiral perturbation of the SmC host by dopant **1** has been based on correlations between δ_p and $1/p$.[14-16] In this paper, we report a more direct assessment of the chiral perturbation exerted by dopant **1** on surrounding host molecules by measuring its effect on the polarization power of other chiral dopants acting as probes.[22] The results of these probe experiments provide the first experimental evidence in support of the CTF model.

Results and Discussion

Chiral Perturbation of the SmC Host. According to the empirical model of Gottarelli et al., the propensity of atropisomeric dopants such as **1** to exert a chiral perturbation via core−core interactions with surrounding host molecules should be a function of the similarity between dopant and host core structures.[18] On the basis of the reasonable assumption that **PhP1** is a better structural match than **PhB** for effective chirality transfer from an atropisomeric biphenyl core, the observation of a 45-fold increase in the polarization power of dopant **1** going from **PhB** (<35 nC/cm^2) to **PhP1** (1555 nC/cm^2) may be rationalized using the CTF model.[14] To test the validity of the CTF model more rigorously, we investigated the perturbation exerted by dopant **1** in **PhP1** and **PhB** by using "reporter" molecules (probes) consisting of chiral dopants which mimic the structures of the two SmC hosts. These probe experiments rely on the reasonable assumption that a perturbation exerted by dopant **1** on the probe/host mixture should cause a variation in the polarization power of the probe (δ_{probe}) that scales with the magnitude of the perturbation. To determine whether the perturbation is achiral or chiral in nature, the polarization power of the probe is measured in the presence of each enantiomer of **1**. If the perturbation is achiral, the two enantiomers should have the same effect on δ_{probe}. On the other hand, if the perturbation is chiral, the two enantiomers should have different effects on δ_{probe} because (+)-**1** and (−)-**1** form diastereomeric pairs with the chiral probe.

The Displaytech dopant **MDW950** and the phenyl benzoate dopant **4** were used as probes in the hosts **PhP1** and **PhB**, respectively. In the first part of each experiment, the polarization power of the probe was measured in the absence of **1** by plotting the reduced polarization (P_o) of SmC* mixtures composed of the probe and SmC host over the mole fraction range $0 \leq x_{\text{probe}} \leq 0.30$. All polarization measurements were done at 5 K below the SmC*−SmA* phase transition temperature ($T - T_C = -5$ K). As shown in Figure 5, the "reference" plots obtained for **MDW950** and **4** give good least-squares fits ($R^2 = 0.997$ and 0.955) with slopes corresponding to δ_{probe} values of -435 ± 11 nC/cm^2 and -62 ± 7 nC/cm^2, respectively (see eq 1).[23] The measurements of P_o as a function of x_{probe} were then repeated in the presence of either (+)-**1** or (−)-**1** at a constant mole fraction $x_1 = 0.04$. To determine the effect of the perturbations exerted by (+)-**1** and (−)-**1** on δ_{probe}, the resulting P_o vs x_{probe} plots are compared to the corresponding reference plots (Figures 6 and 7). For the probe experiments performed in **PhP1**, the reference plot is shifted up and down the y-axis by a value equal to the reduced polarization induced by (+)-**1** and (−)-**1** in the

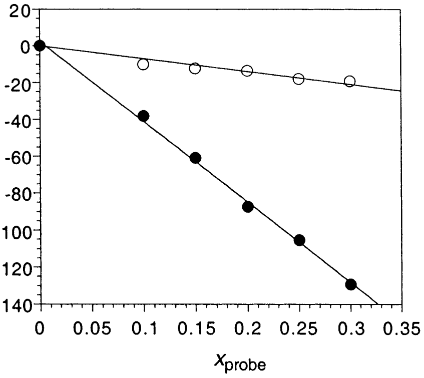

Figure 5. Reduced polarization P_o vs mole fraction of **MDW950** (filled) and **4** (open) in the SmC hosts **PhP1** and **PhB**, respectively, at $T - T_C = -5$ K.

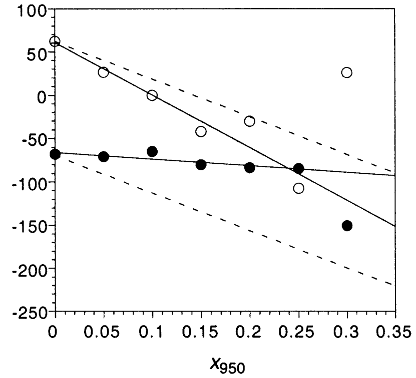

Figure 6. Reduced polarization P_o vs mole fraction of **MDW950** in the SmC host **PhP1** at $T - T_C = -5$ K in the presence of (+)-**1** (open) and (−)-**1** (filled) at a constant mole fraction $x_1 = 0.04$. Each plot represents the average of two duplicate runs which were reproducible within ± 5%. The least-squares fits (solid lines) exclude the data points at $x_{950} = 0.30$. The dashed lines correspond to the least-squares fit of the reference plot for **MDW950** (Figure 5) shifted along the y-axis by a value equal to P_o at $x_{950} = 0$.

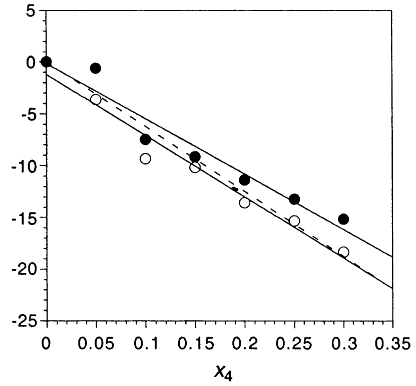

Figure 7. Reduced polarization P_o vs mole fraction of **4** in the SmC host **PhB** at $T - T_C = -5$ K in the presence of (+)-**1** (open) and (−)-**1** (filled) at a constant mole fraction $x_1 = 0.04$. The solid lines correspond to the least-squares fits of the two plots and the dashed line corresponds to the least-squares fit of the reference plot (Figure 5).

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(23) Uncertainty is expressed as the standard error of the least-squares fit of the P_o vs x_{probe} plot.

absence of **MDW950**; no shift is required in **PhB** because $P_o \approx 0$ in the absence of **1**. The shifted reference plots show the results that should be obtained in the absence of perturbation by (+)-**1** and (−)-**1**.

In the phenylpyrimidine host **PhP1**, the P_o vs x_{950} plots obtained in the presence of (+)-**1** and (−)-**1** are approximately linear up to $x_{950} = 0.25$. The deviations from linearity at $x_{950} = 0.30$ are likely due to a cooperative effect between probe molecules that partially counters the perturbation exerted by **1**. If the data points at $x_{950} = 0.30$ are excluded, least-squares fits of the two plots show that the polarization power of **MDW950** increases in the presence of (+)-**1** ($\delta_{probe} = -605 \pm 88$ nC/cm^2) and decreases in the presence of (−)-**1** ($\delta_{probe} = -78 \pm 23$ nC/cm^2).[23] These results reflect the diastereomeric relationship between the two dopant/probe combinations and therefore suggest that dopant **1** exerts a significant chiral perturbation on surrounding **PhP1** molecules.[24] In the phenyl benzoate host **PhBz**, the P_o vs x_4 plots show little deviation from the reference plot. Least-squares fits of the two plots show that the polarization power of **4** decreases slightly in the presence of either (+)-**1** or (−)-**1** ($\delta_{probe} = -59 \pm 5$ nC/cm^2 and -53 ± 6 nC/cm^2, respectively), although statistical analysis using the student *t*-test reveals that these values are not significantly different from the reference δ_{probe} value (vide supra) at the 95% confidence level. These results suggest that dopant **1** does not perturb the host **PhB** and simply behaves as a passive guest, which is consistent with the relatively poor structural match between atropisomeric biphenyl and phenyl benzoate cores to achieve chirality transfer according to the empirical model of Gottarelli and co-workers.[18,19]

Chiral Perturbation of Another Atropisomeric Dopant. The results obtained in the first series of probe experiments strongly suggest that chirality transfer to surrounding host molecules plays an important, if not unique role in amplifying the polarization power of dopant **1** in **PhP1**. However, because the original probe molecules were intended to mimic the SmC host and not the atropisomeric dopant, the question remains whether this amplification is due primarily to a polar ordering of the host or to the CTF effect (Figure 3). The existence of the CTF effect cannot be proven simply by showing that an atropisomeric dopant exerts a chiral perturbation on surrounding host molecules; one must also show that the chiral perturbation exerted by one atropisomeric dopant can amplify the polarization power of another atropisomeric dopant. To solve this problem, we carried out probe experiments in **PhP1** using the methyl-substituted atropisomeric dopant **2** as probe in combination with dopant **1**.

The choice of atropisomeric probe was motivated by a previous study suggesting that dopant **2** exerts a very weak chiral perturbation in **PhP1**.[15] On the basis of conformational analysis and transverse dipole moment calculations, the study predicted that dopant **2** and the isosteric chloro-substituted dopant **3** should exhibit similar polarization powers assuming that they behave as passive guests in the SmC host (i.e., that they exert no perturbation on surrounding host molecules). However, experimental results showed that the polarization power of **3** is more than 4 times that of **2** in **PhP1** (197 nC/cm^2 vs 46 nC/cm^2), which was attributed to the greater propensity of dopant **3** to cause a chiral perturbation in **PhP1**.[25] If this assumption is correct and the CTF effect is a major contributor in **PhP1**, then the purported strong chiral perturbation exerted by dopant **1** should, in principle, amplify the polarization power of one enantiomer of dopant **2** to a value approaching that of **3**. Dopant **2** is also advantageous as a probe molecule because it is unlikely to exert a significant chiral perturbation on dopant **1**.

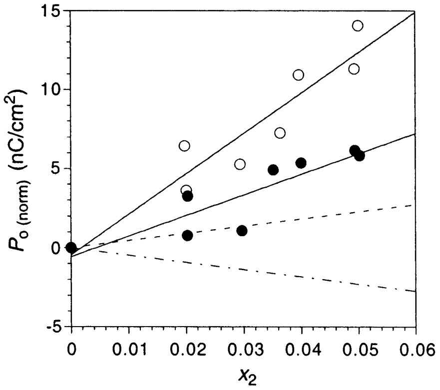

Figure 8. Normalized reduced polarization $P_{o(norm)}$ vs mole fraction of (+)-**2** (open) and (−)-**2** (filled) in the SmC host **PhP1** at $T - T_C = -5$ K in the presence of (+)-**1** at a mole fraction $x_1 = 0.039{-}0.041$. The $P_{o(norm)}$ values are obtained by subtracting the calculated reduced polarization induced by (+)-**1** from the total reduced polarization. The solid lines correspond to the least-squares fits of the two plots and the dashed lines correspond to the least-squares fits of the reference plots for (−)-**2** (−•−) and (+)-**2** (−−−).

The polarization power of each enantiomer (+)-**2** and (−)-**2** was measured in the SmC host **PhP1** in the presence of dopant (+)-**1**. To minimize weighing errors, dopant **2** was mixed with a stock solution of (+)-**1** in **PhP1** ($x_1 = 0.041$) to give SmC* mixtures with mole fractions x_2 ranging from 0 to 0.05 and x_1 ranging from 0.041 to 0.039, respectively. The reduced polarization was measured for each mixture at $T - T_C = -5$ K and the P_o values were normalized by subtracting the calculated P_o contributions from (+)-**1**, taking into account the variations in x_1 caused by dilution, to give the P_o contributions from (+)-**2** and (−)-**2**. The resulting plots of $P_{o(norm)}$ vs x_2 are compared to reference plots previously obtained for (+)-**2** and (−)-**2** in the absence of (+)-**1** (Figure 8).[15] Least-squares fits of the two plots ($R^2 = 0.893$ and 0.776) give δ_{probe} values of $+256 \pm 36$ nC/cm^2 and $+130 \pm 28$ nC/cm^2 for (+)-**2** and (−)-**2**, respectively; the corresponding δ_{probe} values in the absence of (+)-**1** are + 46 and -46 ± 6 nC/cm^2. These results show that the perturbation exerted by (+)-**1** causes the polarization power of (+)-**2** to increase by a factor of 5.5, thus exceeding the polarization power of the dichloro dopant (+)-**3** by 28%.[15] Conversely, the perturbation exerted by (+)-**1** causes an inversion of the sign of P_o induced by (−)-**2** as well as a 2.8-fold increase in the absolute value of δ_{probe}! As in the first series of probe experiments, this remarkable contrast reflects the diastereomeric relationship between the two dopant/probe combinations and strongly suggests that the perturbation exerted by **1** on the probe is chiral in nature.[26] More significantly, the results demonstrate

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[24] In interpreting the probe experiment results, we make the assumption that the perturbation exerted by **1** on surrounding host and probe molecules is the predominant effect. It is likely that the change in composition of the host/probe mixture has an effect on the polarization power of **1** similar to that of a Type II host effect.[11] However, a host effect alone cannot explain the observed deviations from the reference plot because it should affect the polarizations induced by (+)-**1** and (−)-**1** equally.

[25] In the SmC phase of **PhP1**, dopant **3** induces a helical pitch that is ca. 10 times shorter than the that induced by dopant **2** at a constant mole fraction $x_d = 0.02$.[15]

for the first time that a chiral perturbation exerted by one atropisomeric dopant can amplify the polarization power of another atropisomeric dopant, thus providing the first experimental evidence of the chirality transfer feedback effect.

Conclusion

In previous work, we proposed that a chiral perturbation exerted by the atropisomeric dopant **1** is responsible for its unusually high polarization power in the host **PhP1** based on circumstantial evidence derived from correlations between δ_p and the inverse SmC* pitch.[14−16] Experiments using **MDW950** and **4** as probes give additional support to this hypothesis by showing that dopant **1** exerts a much stronger chiral perturbation in **PhP1** than in **PhB**. Furthermore, the results obtained in experiments using the atropisomeric dopant **2** as probe suggest that the chiral perturbation exerted by **1** can amplify the polarization power of another atropisomeric dopants as described by the Chirality Transfer Feedback model. The results of the probe experiments described herein cannot be explained by a polar ordering of the host although this effect probably contributes to some extent to the amplification of δ_p. The development of new probe experiments designed to study the relative contributions of chirality transfer feedback and polar ordering of the host is in progress and will be reported in due course.

Experimental Section

Materials. (*S*,*S*)-5-(2,3-difluorooctyl)-2-(4-octylphenyl)pyridine (**MDW950**) was supplied by Displaytech, Inc. (Longmont, Colorado). 2-(4-Butyloxyphenyl)-5-octyloxypyrimidine (**PhP1**) was obtained from a commercial source. (+)- and (−)-2,2′,6,6′-Tetramethyl-3,3′-dinitro-4,4′-bis[(4-nonyloxybenzoyl)oxy]biphenyl (**1**),[14] (+)- and (−)-2,2′,3,3′,6,6′-hexamethyl-4,4′-bis[(4-nonyloxybenzoyl)oxy]biphenyl (**2**),[15] (*S*)-4-(1-methylheptyloxy)phenyl 4-decyloxybenzoate (**4**),[27] and (±)-4-[(4-methylhexyl)oxy]phenyl 4-decyloxybenzoate (**PhB**)[28] were synthesized according to published procedures and shown to have the expected physical and spectral properties.

Mixture Preparations. Probe Experiments using MDW950 and 4. Two standardized mixtures (6−10 mg) were prepared: a 4.0 mol % mixture of **1** in the probe compound and a 4.0 mol % mixture of **1** in the liquid crystal host. The two standardized mixtures were then combined in various proportions to give liquid crystal mixtures with $0 \leq x_{\text{probe}} \leq 0.30$ and $x_1 = 0.04$.

Probe Experiments using 2. Dopant **2** (0.2 mg) was mixed with samples of a standardized solution of 4.1 mol % of (+)-**1** in **PhP1** ranging in size from 2.0 to 4.5 mg to give liquid crystal mixtures with $0 \leq x_2 \leq 0.05$.

Ferroelectric Polarization Measurements. Texture analyses and transition temperature measurements for the doped liquid crystal mixtures were performed using either a Nikon Labophot-2 POL or Nikon Eclipse E600 POL polarized microscope fitted with a Linkam LTS 350 hot stage. Spontaneous polarizations (P_S) were measured at 5 K below the SmA*-SmC* phase transition temperature ($T - T_C = -5$ K) by the triangular wave method[29] (6V/μm, 80−100 Hz) using a Displaytech APT-III polarization testbed in conjunction with the Linkam hot stage. Polyimide-coated ITO glass cells (4 μm × 0.25 cm^2) supplied by Displaytech Inc. were used for all the measurements. Good alignment was obtained by slow cooling of the filled cells from the isotropic phase via the N* and SmA* phases. Tilt angles (θ) were measured at $T - T_C = -5$ K between crossed polarizers as half the rotation between two extinction positions corresponding to opposite polarization orientations. The sign of P_S along the polar axis was assigned from the relative configuration of the electrical field and the switching position of the sample according to the established convention.[5] Reduced polarization (P_o) values were then obtained as $P_S/\sin\theta$.[8]

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(26) In principle, the results obtained with **2** as chiral probe could be explained by a host effect causing the polarization power of (+)-**1** to increase proportionally with x_2, and resulting in an upward shift of the two reference plots. However, this would be inconsistent with previous studies showing that the polarization power of **1** tends to decrease when various achiral additives are mixed with **PhP1**. Vizitiu, D., Ph.D. Thesis, Queen's University, 1999.

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