

Chiral Distortion of the Binding Site in a Ferroelectric Liquid Crystal Induced by an Atropisomeric Biphenyl Dopant

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Ferroelectric liquid crystals hold tremendous potential in high-resolution microdisplay applications due to their fast response time, wide viewing angle and bistability.^{1–3} Commercial FLC mixtures for display applications are normally obtained by mixing small amounts of a chiral dopant with high polarization power δ_p into an achiral SmC host mixture with low viscosity and wide temperature range.⁴ Thus, an important aspect of FLC research over the past 15 years has focused on understanding the relationship between the molecular structure of a chiral dopant and the magnitude of the spontaneous polarization, P_S , it induces.^{5,6} According to the Boulder model for the molecular origins of P_S , the orientational and conformational ordering of a chiral dopant in a SmC host can be modeled by a mean-field potential which qualitatively behaves like a binding site analogous to that described in organic host–guest chemistry and biochemistry.^{5,7,8} Within the confines of this binding site, which is shaped like a bent cylinder with C_{2h} symmetry, the orientational distribution of a molecule along its long axis acquires a polar character. In the case of a chiral dopant, steric coupling to the stereocenter(s) causes a desymmetrization of the conformational energy hypersurface which, in combination with the polar orientational ordering imposed by the binding site, results in an orientational bias of the dopant's transverse dipole moment along the polar C_2 axis (i.e., a spontaneous polarization).

Recently, we reported that chiral dopants with an atropisomeric biphenyl core (e.g., **1**) have polarization powers which depend very strongly on the core structure of the SmC host (Type II host

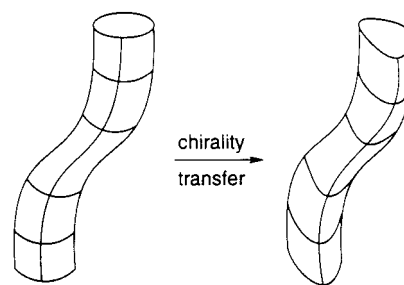
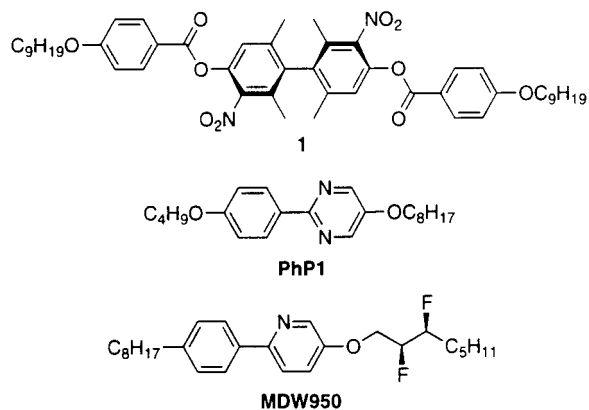


Figure 1. Chiral distortion of the SmC binding site.

effect).⁹ For example, δ_p values for **1** range from <30 nC/cm² in a phenyl benzoate host to 1555 nC/cm² in the phenylpyrimidine host **PhP1**.¹⁰ This host effect may be viewed as a manifestation of molecular recognition which cannot be achieved with more conventional dopants with chiral tails due to the higher degree of conformational disorder among side-chains in the SmC phase. Indeed, measurements of δ_p as a function of the length of the dopant side-chains showed that the polarization induced in **PhP1** is uniquely sensitive to the positional ordering of the atropisomeric core with respect to the core sublayer of the SmC host.⁹ We also showed that an inverse relationship exists between δ_p and the helical pitch of the induced SmC* phase, which suggests that chirality transfer to surrounding SmC host molecules contributes to the induction of high polarizations in **PhP1**.¹¹ To explain these results, we proposed that chirality transfer via core–core interactions causes a *chiral distortion of the SmC binding site* (Figure 1) which, in turn, increases the orientational bias of the atropisomeric dopant along the polar C_2 axis by virtue of diastereomeric relationships between the chiral conformations of the dopant and the chiral binding site (i.e., a chirality transfer feedback (CTF) mechanism).⁹ In this work, we present the first experimental evidence of a chiral distortion of the binding site in a SmC* liquid crystal phase induced by dopant **1**.



The approach taken in this study is to measure the effect of dopant **1** on the polarization induced by a second chiral dopant (probe) which mimics the structure of the host **PhP1**. The Displaytech compound **MDW950** was selected as probe dopant because (i) it possesses a core structure similar to that of **PhP1**

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(1) (a) Lagerwall, S. T. In *Ferroelectric and Antiferroelectric Liquid Crystals*; Wiley-VCH: Weinheim, 1999. (b) Lagerwall, S. T. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, pp 515–664.

(2) Walba, D. M. *Science* **1995**, *270*, 250.

(3) Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric Liquid Crystals: Principles, Properties and Applications*; Gordon & Breach: Philadelphia, 1991.

(4) The polarization power measures the propensity of a chiral dopant to induce a spontaneous polarization P_S according to the equation: $\delta_p = (dP_o(x_d)/dx_d)_{x_d \rightarrow 0}$ where x_d is the dopant mole fraction and P_o is the reduced polarization of the SmC* phase. Siemensmeyer, K.; Stegemeyer, H. *Chem. Phys. Lett.* **1988**, *148*, 409. The reduced polarization is normalized for variations in tilt angle θ and is equal to $P_S/\sin \theta$. Kuczynski, W.; Stegemeyer, H. *Chem. Phys. Lett.* **1980**, *70*, 123.

(5) Walba, D. M. In *Advances in the Synthesis and Reactivity of Solids*; Mallouck, T. E., Ed.; JAI Press, Ltd.: Greenwich, CT, 1991; Vol. 1; pp 173–235.

(6) (a) Goodby, J. W.; Chin, E.; Leslie, T. M.; Geary, J. M.; Patel, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 4729. (b) Goodby, J. W.; Chin, E. *J. Am. Chem. Soc.* **1986**, *108*, 4736.

(7) Glaser, M. A.; Ginzburg, V. V.; Clark, N. A.; Garcia, E.; Walba, D. M.; Malzbender, R. *Mol. Phys. Rep.* **1995**, *10*, 26.

(8) Glaser, M. A. In *Advances in the Computer Simulations of Liquid Crystals*; Zannoni, C., Pasini, P., Ed.; Kluwer: Dordrecht, 1999; pp 263–331.

(9) Vizitium, D.; Lazar, C.; Halden, B. J.; Lemieux, R. P. *J. Am. Chem. Soc.* **1999**, *121*, 8229.

(10) Polarization power measurements were carried out with dopant mole fractions ranging from $x_1 = 0.005$ to $x_1 = 0.05$.

(11) The term *chirality transfer* refers to the induction of chiral conformations in the core structures of surrounding SmC host molecules. A similar mechanism of chirality transfer was proposed by Gottarelli et al. for cholesteric phases induced by atropisomeric biaryl dopants. Gottarelli, G.; Hibert, M.; Samori, B.; Solladié, G.; Spada, G. P.; Zimmermann, R. *J. Am. Chem. Soc.* **1983**, *105*, 7318.

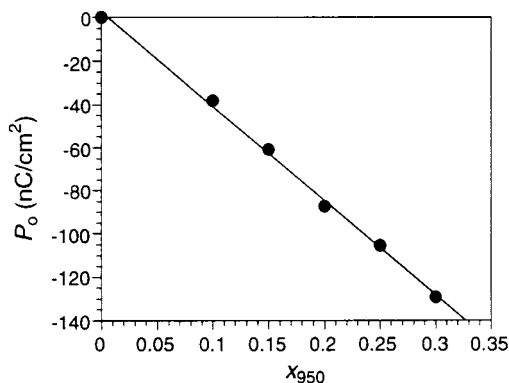


Figure 2. Reduced polarization P_0 vs mole fraction of MDW950 x_{950} in the SmC host PhP1 at $T - T_C = -5$ K.

and is therefore equally susceptible to chirality transfer via core–core interactions with **1**, (ii) it is highly miscible in phenylpyrimidine SmC hosts such as PhP1, and (iii) it induces a high spontaneous polarization. In the first part of the experiment, we obtained a reference plot by measuring the reduced polarization (P_0) of SmC* mixtures composed of the probe dopant MDW950 and PhP1 over the mole fraction range $0 \leq x_{950} \leq 0.30$.¹² As shown in Figure 2, the reference plot gives an excellent least-squares fit ($R^2 = 0.997$) from which a polarization power of -435 nC/cm² is derived.⁴ In the second part of this experiment, the P_0 measurements which gave the reference plot were repeated in the presence of either (+)-**1** or (–)-**1** at a constant mole fraction $x_1 = 0.04$.¹³ If the atropisomeric dopant has little or no chiral influence on the surrounding host molecules, the polarizations induced by **1** and MDW950 should be additive and produce linear P_0 versus x_{950} plots with the same slope as the reference plot but shifted positively or negatively by a value corresponding to P_0 induced by (+)-**1** or (–)-**1**. On the other hand, if the atropisomeric dopant causes a chiral distortion of the binding site, the resulting P_0 vs x_{950} plots should deviate from the reference plot due to the influence of the chiral distortion on the orientational bias of the chiral 2,3-difluorooctyloxy side-chain in MDW950.¹⁴

Measurements of P_0 versus x_{950} in the presence of (+)-**1** and (–)-**1** were carried out in duplicate and gave reproducible results within $\pm 5\%$. The resulting P_0 versus x_{950} plots were found to deviate significantly from the reference plot (see Supporting Information). Such deviation is due in part to an achiral contribution of the Type II host effect as the SmC host composition changes from pure PhP1 to $\sim 70:30$ PhP1/MDW950.¹⁵ To determine the extent of this achiral host effect, we repeated one series of measurements with $x_1 = 0.04$ using a racemic mixture of the probe dopant instead of the enantiomerically pure MDW950. The result of this control experiment showed that the magnitude of P_0 induced by **1** gradually decreases with increasing

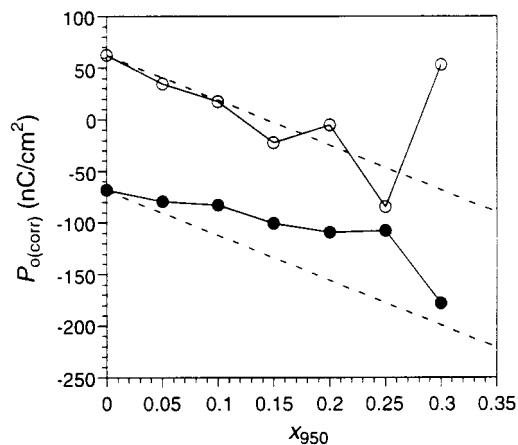


Figure 3. Corrected reduced polarization $P_{0(\text{corr})}$ vs mole fraction of MDW950 x_{950} in the SmC host PhP1 at $T - T_C = -5$ K in the presence of (+)-**1** (open circles) and (–)-**1** (filled circles) at a constant mole fraction $x_1 = 0.04$. The correction accounts for an achiral contribution of the Type II host effect. The dashed lines correspond to the least-squares fit from Figure 2 shifted by $P_{0(\text{corr})}$ at $x_{950} = 0$. Each plot represents the average of two duplicate runs, which were reproducible within $\pm 5\%$.

mole fraction of racemic probe dopant, but it cannot fully account for the deviations observed in the P_0 versus x_{950} plots. The P_0 values measured in the probe experiments were corrected for the achiral host effect by subtracting the corresponding negative deviations in P_0 measured in the control experiment to give the plots shown in Figure 3. For the (+)-**1**/MDW950 dopant combination, the corrected plot does not deviate appreciably from the reference plot until $x_{950} = 0.30$ is reached, at which point a large positive deviation (by 175% of the reference value) is observed. For the (–)-**1**/MDW950 dopant combination, a more gradual, yet significant, negative deviation from the reference plot (by as much as 40% of the reference value) is observed, starting at $x_{950} = 0.05$.

The observed deviations from the reference plot, and the absence of reflection symmetry between the corrected (+)-**1**/MDW950 and (–)-**1**/MDW950 plots strongly suggest that the atropisomeric dopant causes a chiral distortion of the binding site—the two enantiomers (+)-**1** and (–)-**1** form diastereomeric pairs with MDW950 which must be energetically nonequivalent in terms of their chiral interactions. Furthermore, the nonlinear aspect of the corrected P_0 versus x_{950} plots suggests that some cooperative effect may result from chirality transfer to MDW950 which may be unique to the structure of the probe dopant. Further studies aimed at understanding the nature of such nonlinear effect and establishing the generality of the CTF mechanism in the induction of FLC phases using atropisomeric dopants are in progress.

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Supporting Information Available: Uncorrected plots of P_0 vs x_{950} in the presence of (+)-**1** and (–)-**1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Spontaneous polarizations (P_S) were measured at 5 K below the SmC*–SmA* phase transition temperature ($T - T_C = -5$ K) by the triangular wave method (6 V/ μm , 80 – 100 Hz) using a Displaytech APT-III polarization testbed in conjunction with a Linkam LTS350 hot stage. Miyasato, K.; Abe, S.; Takezoe, H.; Fukuda, A.; Kuze, E. *Jpn. J. Appl. Phys.* **1983**, *22*, L661. Polyimide-coated ITO glass cells (4 $\mu\text{m} \times 0.25$ 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 as a function of temperature 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_0) values were obtained as $P_S/\sin \theta$.⁴

(13) Dopants (–)-**1** and (+)-**1** were obtained in enantiomerically pure (>99% ee) and near-enantiomerically pure (92% ee) form, respectively, by chiral stationary phase HPLC resolution of the dihydroxybiphenyl precursor using a Daicel Chiralcel OJ semi-prep column.⁹ Samples of PhP1 and MDW950 were each doped with (+)-**1** or (–)-**1** at $x_1 = 0.04$ and mixed in various proportions to cover the range $0 \leq x_{950} \leq 0.30$.

(14) (a) Thurmes, W. N.; Wand, M. D.; Vohra, R. T.; More, K. M.; Walba, D. M. *Liq. Cryst.* **1993**, *14*, 1061. (b) Wand, M. D.; Vohra, R.; Walba, D. M.; Clark, N. A.; Shao, T. *Mol. Cryst. Liq. Cryst.* **1991**, *202*, 183.

(15) Stegemeyer proposed that the Type II host effect is due in part to variations in rigid core–core interactions between chiral dopant and SmC host molecules that result in a change in the orientational distribution of the dopant transverse dipole with respect to the polar C_2 axis. Stegemeyer, H.; Meister, R.; Hoffmann, U.; Sprick, A.; Becker, A. *J. Mater. Chem.* **1995**, *5*, 2183. This *biaxial ordering* model, which does not consider the effect of chirality transfer, and the CTF model are not mutually exclusive, and both can contribute to the Type II host effect. Previous work in our laboratory has shown that the polarization power of dopant **1** can be modified by simply varying the ratio of two achiral phenylpyrimidine SmC hosts. Vizitru, D. Ph.D. Thesis, Queen's University, 1999.