

Ferroelectric liquid crystal induced by a bridged biphenyl dopant with helical topography

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A new atropisomeric dopant containing a bridged biphenyl core with helical topography, 3,9-bis[(4-nonyloxy)benzoyloxy]-5,7-dihydro-1,11-dinitrodibenz[*c,e*]thiepin (**2**), was synthesized in optically pure form and doped in the liquid crystal host 2-(4-butyloxyphenyl)-5-octyloxy pyrimidine (**PhP1**) to produce a ferroelectric SmC* phase. The polarization power δ_p of this new dopant is compared to that of an analogous unbridged dopant, 2,2'-dimethyl-6,6'-dinitro-4,4'-bis[(4-*n*-nonyloxy)benzoyloxy]biphenyl (**1**), after normalizing for a difference in core transverse dipole moments. Results show that the normalized polarization power of the bridged dopant **2** is greater than that of the unbridged dopant **1** by a factor of 5.3. On the other hand, the SmC* helical pitch p induced by **2** is shorter than that induced by **1** by a factor of 1/6.7. This inverse relationship is consistent with predictions that dopant **2** should have a greater propensity to undergo chirality transfer with surrounding host molecules *via* conformational core–core interactions. A more direct assessment of the chiral perturbation exerted on the host molecules is achieved by studying the effects of dopants **1** and **2** on the spontaneous polarization induced by a probe chiral dopant, (*S,S*)-5-(2,3-difluorooctyl)-2-(4-octylphenyl)pyridine (**MDW950**), which mimics the structure of **PhP1**.

Introduction

Liquid crystals are anisotropic fluids with bulk properties that can be readily influenced by the presence of non-mesogenic additives (dopants). Liquid crystal chiral bulk properties such as the helical structures of the chiral nematic (N*) and chiral smectic C (SmC*) phases, and the spontaneous polarization (P_s) of the SmC* phase can be induced by small amounts of chiral dopant.¹ In the case of an induced N* phase, the helical twisting power (β_M) of a chiral dopant is generally a function of the structural similarity between the chiral dopant and the nematic liquid crystal host, which is consistent with an empirical model proposed by Gottarelli *et al.* for chirality transfer *via* chiral conformational interactions.² In the case of an induced SmC* phase, the polarization power (δ_p) of a conventional dopant with chiral side-chain(s) is generally independent of the structure of the achiral SmC liquid crystal host (Type I).^{3,4} However, recent studies have shown that less conventional dopants with chiral cores exhibit polarization powers that depend strongly on the structure of the SmC host (Type II).^{4–8} This host effect is thought to arise from core–core interactions between the chiral dopant and surrounding host molecules, and may be viewed as a manifestation of molecular recognition similar to that influencing the induction of chiral nematic phases.^{7,8} In this paper, we present new evidence supporting this view based on the propensity of a bridged biphenyl dopant with helical topography to induce a spontaneous polarization in a phenylpyrimidine SmC host.

Chiral dopants containing an atropisomeric biphenyl core with a large transverse dipole moment exhibit unusually high polarization powers in the phenylpyrimidine host **PhP1**.^{6–8} Previous studies have shown that the polarization power is uniquely sensitive to the positional ordering of the

atropisomeric core with respect to the core sublayer of the SmC host,⁷ and that an inverse relationship exists between δ_p and the helical pitch of the SmC* phase in **PhP1**.^{7,8} These results suggest that δ_p is a function of the degree of chiral perturbation exerted by atropisomeric dopants on surrounding SmC host molecules *via* a form of core–core conformational interaction similar to that postulated by Gottarelli *et al.* for chirality transfer in a nematic liquid crystal phase (Fig. 1).²

Previous studies of chiral induction in cyanobiphenyl nematic liquid crystals have shown that bridged biphenyl and binaphthyl dopants with helical topography exhibit higher helical twisting powers than the corresponding unbridged dopants, and that the magnitude of β_M is dependent on the

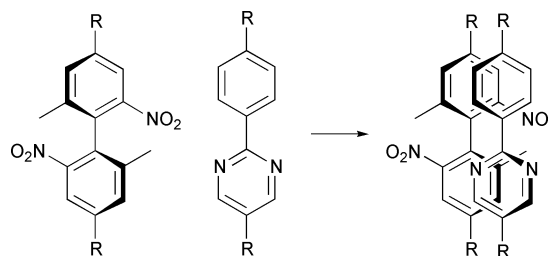
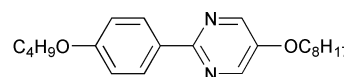
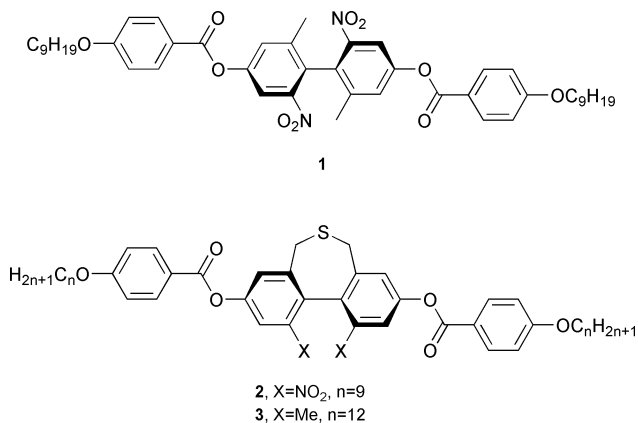


Fig. 1 Model for chirality transfer *via* core–core interactions between the atropisomeric dopant **1** and the SmC host **PhP1**.



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

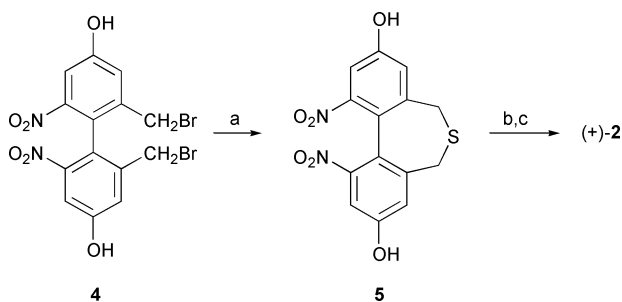


torsional angle formed by the planes of the two aromatic rings.^{2,9–11} This structure–property relationship is consistent with the empirical model of Gottarelli *et al.* and was confirmed by theoretical predictions based on the surface tensor mean field model of Nordio and Ferrarini.¹² This is also consistent with a recent classical theoretical analysis of chiral induction in nematic phases which considers the biaxiality of the chiral dopant and biaxial correlations between molecules.¹³ Hence, if a similar form of chirality transfer contributes to the induction of high spontaneous polarizations in the SmC host **PhP1**, we expect a bridged biphenyl dopant to exhibit a higher polarization power than the corresponding unbridged dopant. To test this hypothesis, we synthesized the dopant 3,9-bis[(4-nonyloxy)benzoyloxy]-5,7-dihydro-1,11-dinitrodibenz[*c,e*]thiepin (**2**) and compared its polarization power in **PhP1** to that of 2,2'-dimethyl-6,6'-dinitro-4,4'-bis[(4-*n*-nonyloxy)benzoyloxy]biphenyl (**1**).¹⁴ In a recent study, Solladié *et al.* showed that the bridged biphenyl compound **3** forms a chiral SmC* phase, but reported no polarization measurement.¹⁵ The mesomorphic character of **3** was attributed primarily to the presence of the sulfide bridge, which reduces the torsional angle formed by the planes of the two aromatic rings and increases the biaxiality of the core relative to an unbridged, non-mesogenic biphenyl derivative such as **1**.¹⁶

Results

Synthesis and characterization

Compound **2** was obtained in racemic form by treatment of the known dibromide precursor **4** with Na₂S·9H₂O in MeOH–H₂O, followed by esterification with the corresponding acid chloride (Scheme 1). Resolution of (±)-**2** was achieved on a semi-prep scale by chiral stationary phase (CSP) HPLC on an (*S,S*)-Whelk-O1 column to give (+)-**2** and (–)-**2** in optically pure forms. Interestingly, compound **2** does not form a liquid crystal phase despite a 28° reduction in the torsional angle formed by the planes of the two aromatic rings according to B3LYP/6-31G(d) calculations—the torsional angle defined by



Scheme 1 Reagents and conditions: a) Na₂S·9H₂O, 10 : 1 MeOH–H₂O, Δ; (b) 4-nonyloxybenzoyl chloride, DMAP, THF; (c) CSP HPLC resolution, (*S,S*)-Whelk-O1 column, 8 : 2 hexanes–IPA, 5 mL min^{–1}.

C-6, C-1, C-1' and C-6' in dopant **1** is 92° and the corresponding torsional angle defined by C-1, C-11b, C-11a and C-11 in dopant **2** is 64°.

Ferroelectric polarization and helical pitch measurements

The optically pure compounds (–)-**1** and (+)-**2** were doped in the host **PhP1** over the mole fraction range 0.02 < *x*_d < 0.04 to produce chiral SmC* phases. Alignment of the SmC* mixtures in polyimide-coated ITO glass cells with a 4 μm spacing produced surface-stabilized FLC films suitable for measurement of ferroelectric properties.¹⁷ Spontaneous polarizations and tilt angles were measured at 5 K below the SmC*–SmA* phase transition temperature (*T* – *T*_C = –5 K) by the triangular wave method¹⁸ and the corresponding *P*₀ values were derived according to Stegemeyer *et al.*³ Plots of *P*₀ vs. *x*_d gave good linear fits (*R*² = 0.963–0.994) from which δ_p values were derived (Table 1). To study the influence of chiral perturbations of the SmC host on δ_p, the helical pitch *p* of SmC* phases induced by (–)-**1** and (+)-**2** in **PhP1** was measured by polarized light microscopy at a constant dopant mole fraction *x*_d = 0.02 (Table 1). The inverse pitch is taken as a measure of intermolecular chirality transfer in the SmC* phase.^{7,8}

Conformational analyses

To assess the influence of core topography on the polarization power of the two dopants in **PhP1**, it is necessary to normalize δ_p values with respect to differences in conformational asymmetry and transverse dipole moment (μ_⊥) of the atropisomeric cores. Polar ordering of dopants such as **1** and **2** is thought to originate from a small asymmetric bias in the energy profile for rotation of the rigid biphenyl core with respect to the two ester side-chains, which should result in a preferred orientation of the core transverse dipole moment along the polar axis of the SmC* phase (Fig. 2).^{6,7} Accordingly, energy profiles for rotation about the ester C–O bond in substructures **6** and **7** were calculated as a function of the dihedral angle defined by atoms 1–2–3–4 (φ₁) at 15° intervals over the range 0° ≤ φ₁ ≤ 345° (the numbering scheme used in substructures **6** and **7** does not conform to IUPAC nomenclature and is used for the sake of clarity). For each conformation, the dihedral angle φ₁ was constrained to its predetermined value and the dihedral angle defined by atoms 3–4–5–6 (φ₂) was fixed at 0°.¹⁹ The structure was then optimized using the RHF/6-31G(d) method,²⁰ followed by a single-point energy calculation using Becke's hybrid density functional with the Lee–Yang–Parr correlation functional (B3LYP)²¹ and the 6-31G(d) basis set.

A comparison of the two energy profiles shown in Fig. 3 suggests that the conformational bias giving rise to a preferred orientation of the core transverse dipole moment along the polar axis should not change appreciably upon bridging the biphenyl core. These results also suggest that the ester groups in **1** and **2** make similar contributions to μ_⊥ and can be ignored in normalizing the polarization power. Hence, transverse dipole moments were calculated at the B3LYP/6-31G(d) level for the minimized core structures of **1** and **2** without the two ester

Table 1 Polarization power δ_p and normalized polarization power δ_{p(norm)} of dopants (–)-**1** and (+)-**2** and helical pitch *p* of the SmC* phases induced in the host **PhP1**

Dopant	μ _⊥ /D ^a	δ _p /nC cm ^{–2b,c}	δ _{p(norm)} /nC cm ^{–2 D^{–1}}	<i>p</i> /μm ^{d,e}
(–)- 1	5.65	106 ± 15 (+)	18.8	95.8 ± 6.8
(+)- 2	4.67	463 ± 23 (+)	99.1	14.2 ± 0.8

^aCalculated at the B3LYP/6-31G(d) level for the minimized core structures of **1** and **2** without ester groups. ^bSign of induced *P*_S in parentheses. ^cUncertainty is ± standard error of least-squares fit. ^dMeasured at a dopant mole fraction *x*_d = 0.02. ^eUncertainty is ± one standard deviation.

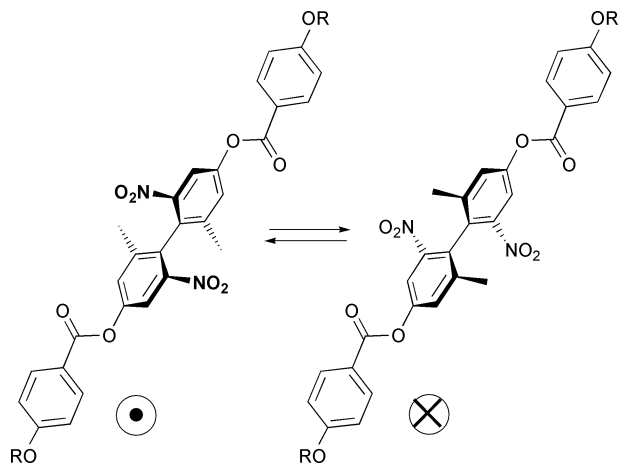


Fig. 2 Rotation of the atropisomeric core about the two ester C–O bonds of dopant **1** in the SmC* phase. The polar C_2 axis is normal to the plane of the page and the direction of the core transverse dipole moment along that axis is shown for each conformation.

groups. The δ_p values were then divided by the calculated transverse dipole moments to give normalized $\delta_{p(\text{norm})}$ values.

Probe experiments

For a more direct assessment of the chiral perturbation exerted on the host molecules, we studied the effects of dopants **1** and **2** on the spontaneous 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 **PhP1** and is therefore equally susceptible to chirality transfer *via* core–core interactions, and (ii) it is highly miscible in the host **PhP1**. To carry out these experiments, a reference plot was first obtained by measuring the reduced polarization (P_o) of SmC* mixtures composed of **MDW950** and **PhP1** over the mole fraction range $0 \leq x_{950} \leq 0.30$. The P_o vs. x_{950} reference plot gave an excellent least-squares fit ($R^2 = 0.997$) from which a polarization power of -435 nC cm^{-2} for **MDW950** was derived.²² The measurements of P_o as a function of x_{950} were then repeated in the presence of an atropisomeric dopant at a constant mole fraction $x_d = 0.04$. Probe experiments were carried out for dopants (+)-**1**, (–)-**1**, (+)-**2** and (–)-**2**, and the resulting P_o vs. x_{950} plots are shown in Fig. 4. In each case, the P_o vs. x_{950} plot 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 **MDW950**. The shifted reference plots represent the results expected if the polarizations induced by the atropisomeric dopant and **MDW950** are additive, *i.e.*, if the dopant does not perturb the probe–host mixture. To confirm the results shown in Fig. 4, we repeated the four probe experiments using a racemic mixture of the

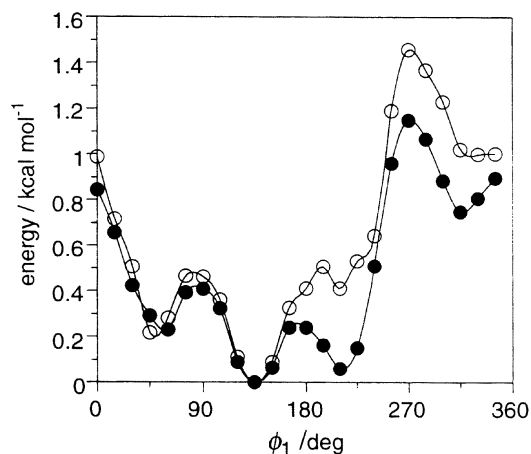
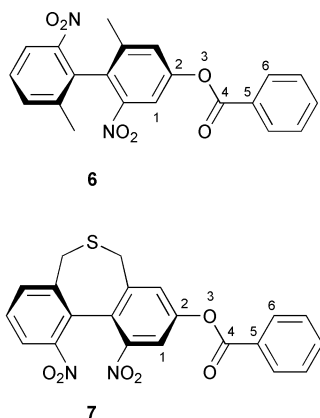


Fig. 3 Relative energy in kcal mol^{-1} as a function of the torsional angle ϕ_1 defined by atoms 1, 2, 3 and 4 in structures **6** (○) and **7** (●) according to B3LYP/6-31G(d) calculations.

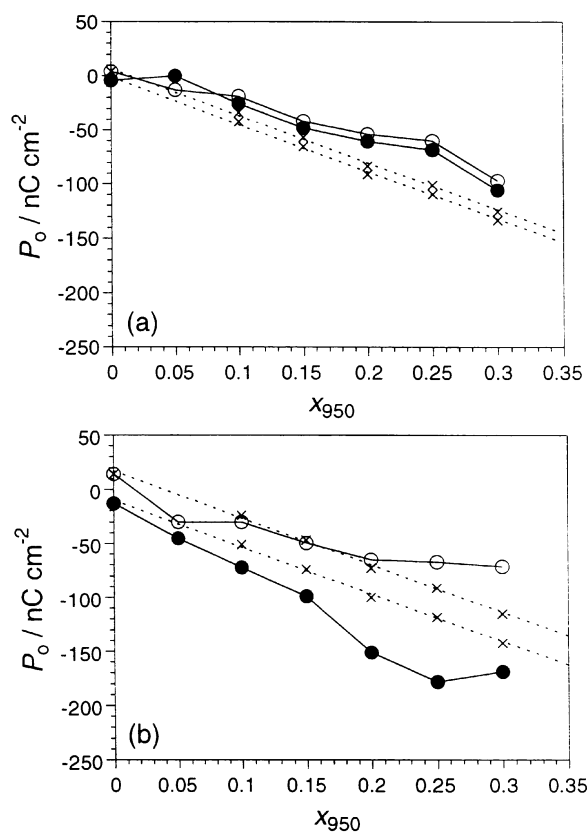


Fig. 4 (a) Reduced polarization P_o vs. mole fraction of the probe dopant **MDW950** x_{950} in the SmC host **PhP1** at $T - T_C = -5 \text{ K}$ in the presence of (–)-**1** (○) and (+)-**1** (●) at a constant mole fraction $x_1 = 0.04$, and (b) in the presence of (–)-**2** (●) and (+)-**2** (○) at a constant mole fraction $x_2 = 0.04$. In both figures, plots of P_o vs. x_{950} in the absence of atropisomeric dopant (×) are shifted along the y -axes by values corresponding to P_o measured in the presence of atropisomeric dopant at $x_{950} = 0$. The dashed lines correspond to the least-squares fit ($R^2 = 0.997$).

probe dopant instead of the optically pure form. The resulting plots of P_o vs. x_{rac} are shown in Fig. 5.

Discussion

The Type II host effect

A comparison of the data in Table 1 suggests that core topography exerts a striking influence on the polarization

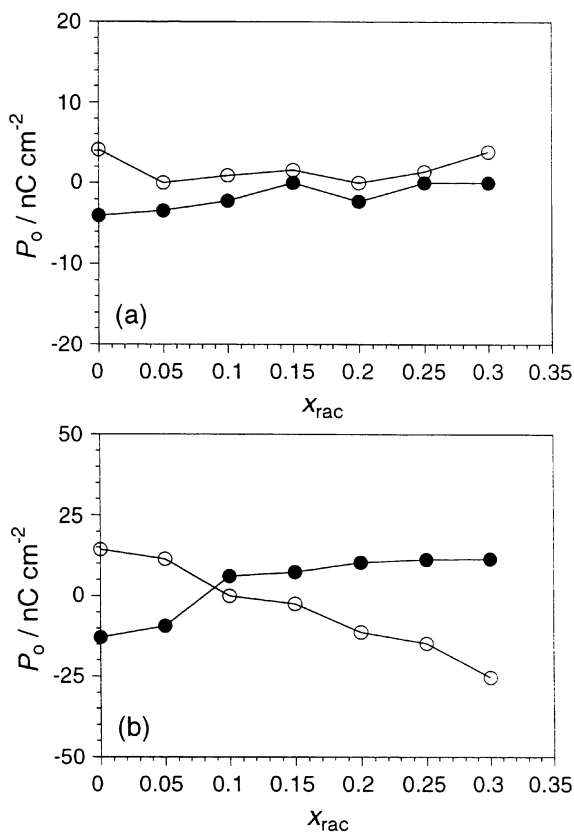


Fig. 5 (a) Reduced polarization P_0 vs. mole fraction of the racemic probe dopant x_{rac} in the SmC host **PhP1** at $T - T_C = -5$ K in the presence of (–)-**1** (○) and (+)-**1** (●) at a constant mole fraction $x_1 = 0.04$, and (b) in the presence of (–)-**2** (●) and (+)-**2** (○) at a constant mole fraction $x_2 = 0.04$.

power of atropisomeric dopants in the host **PhP1**. In order to understand the nature of this influence, we need to consider current models for the origins of the host effect observed with Type II dopants. 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 organic host–guest chemistry and biochemistry.^{23,24} The mean field potential is approximately C_{2h} -symmetric and has a zig-zag shape so that the molecular side-chains are, on average, less tilted with respect to the smectic layer normal than is the molecular core.²⁵ When a chiral dopant is confined to this binding site, molecular orientations related by a 180° rotation about the molecular long axis are no longer energetically equivalent. The orientational ordering imposed by the binding site, in combination with the conformational asymmetry of the chiral dopant, results in an orientational bias of the transverse dipole moment along the polar C_2 axis (polar ordering) which gives a spontaneous polarization.

As a first approximation, the Boulder model assumes that a chiral dopant plays the role of a *passive* guest which must adopt a particular conformation and orientation that best “fits” the binding site of the host. In the case of a conventional Type I dopant, the shape of the binding site is assumed to be invariant with the SmC host structure. This is consistent with a low degree of conformational rigidity in the side-chain region of the SmC layer that precludes any molecular recognition by the chiral side-chain of the dopant. On the other hand, the Type II host effect may be viewed as a manifestation of molecular recognition by the chiral core of the dopant through core–core interactions with surrounding host molecules, and is consistent with a higher degree of conformational rigidity in the core

region of the SmC layer.

$$\delta_p = \frac{N_1}{x_d} \mu_{\perp} \frac{a_1}{2kT} \cos \psi_0 \quad (1)$$

Stegemeyer explained the Type II host effect using mathematical expressions such as eqn. (1) that include two key terms: (i) a *polar ordering* term (a_1) that is a function of the conformational asymmetry of the chiral dopant, and (ii) a *rotational distribution* term ($\cos \psi_0$) that describes the orientation of the dopant transverse dipole moment μ_{\perp} with respect to the polar axis.⁴ N_1 and x_d represent the number density and mole fraction of dopant molecules, respectively. According to one 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 polarization in one host if μ_{\perp} is oriented near the tilt plane (Fig. 6a), and a high polarization in another host if μ_{\perp} is oriented near the polar axis (Fig. 6b). This explanation may be reconciled with the passive guest assumption of the Boulder model by postulating that the central part of the binding site changes shape from one host to the next while maintaining reflection symmetry.

In another microscopic model, Stegemeyer suggested that intermolecular chirality transfer can contribute to the Type II host effect by causing a polar ordering of the host, thus inducing an additional polarization that scales with the transverse dipole moment of the host molecule.⁴ In the present case, however, the phenylpyrimidine core of **PhP1** is unlikely to contribute to P_S as a result of chirality transfer. As an alternative, we recently proposed a different model—the Chirality Transfer Feedback (CTF) model—in which a Type II dopant plays the role of an *active* guest and causes a chiral distortion of the binding site *via* chirality transfer to surrounding host molecules (Fig. 7).⁷ As a feedback, this chiral distortion can increase the polar ordering of the dopant by causing a shift in the conformational equilibrium of the chiral core (e.g., Fig. 2). This shift occurs by virtue of the diastereomeric relationships between “host–guest complexes”

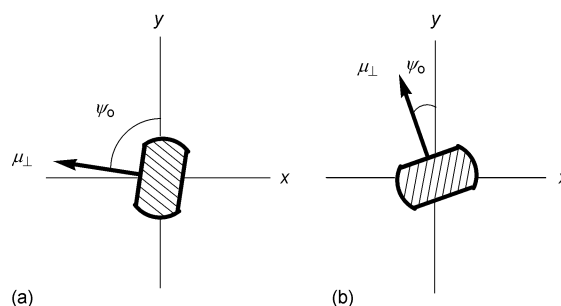


Fig. 6 Two different rotational distributions of a Type II chiral dopant viewed along the long molecular axis. The y -axis corresponds to the polar axis and the xz -plane corresponds to the smectic tilt plane.

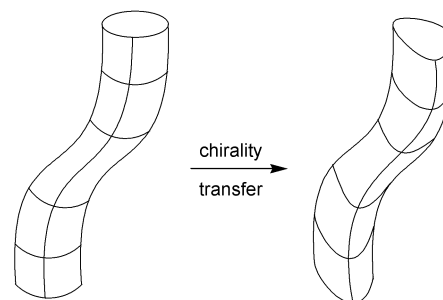


Fig. 7 Chiral distortion of the binding site according to the CTF model.

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 μ_{\perp} towards the polar axis.

Correlation with the helical pitch

The helical structure of the chiral SmC* phase is thought to originate from the internal molecular twist of chiral mesogens and/or dopants. The molecular twist of a chiral dopant may be propagated to surrounding host molecules through excluded volume interactions, and then from one smectic layer to the next by virtue of the substantial interlayer mixing existing at the layer interfaces.^{26,27} According to this model, the pitch p of the SmC* helix is a function of the molecular length and the displacement angle α describing the molecular twist of the chiral molecule when viewed end-on (Fig. 8). An analysis of space-filling models (AM1) reveals that dopants **1** and **2** in their lowest energy conformations have the same molecular length (43.4 Å), and displacement angles α of 7.4° and 5.4°, respectively. This suggests that dopant **1** should induce a shorter helical pitch than **2** if the dopant molecular twist is propagated to surrounding host molecules through excluded volume interactions only. However, the dopant molecular twist may also be propagated through the induction of homochiral core conformations in host molecules, as described in Fig. 1, which should be more efficient with dopant **2** according to empirical and theoretical models.^{2,12,13} The results in Table 1 are consistent with this reasoning. Furthermore, the inverse relationship between $\delta_{p(\text{norm})}$ and p suggests that the increase in polarization power may be due in large part to a greater propensity of dopant **2** to behave as an active guest according to the CTF model.

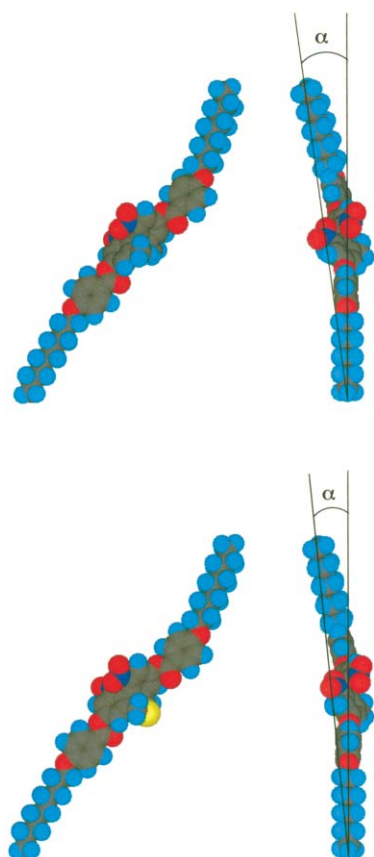


Fig. 8 Side-on and end-on views of space filling models of dopants **1** (top) and **2** (bottom) generated by semi-empirical calculations at the AM1 level. In each case, the torsional angle ϕ_1 was constrained to the value corresponding to the global energy minimum calculated at the B3LYP/6-31G(d) level.

Analysis of the probe experiments

The probe experiments rely on the assumption that any perturbation exerted by an atropisomeric dopant on the probe–host mixture should influence the polar ordering and/or rotational distribution of the probe molecule and cause a deviation of the corresponding P_o vs. x_{probe} plot from the reference plot. To determine whether a perturbation is achiral or chiral in nature, plots obtained with each enantiomer of the atropisomeric dopant are compared. If a perturbation is achiral, the deviations should be identical and the two plots should be superposable; if a perturbation is chiral, the two plots should be non-superposable because the two enantiomers of the dopant form non-equivalent diastereomeric pairs with **MDW950**.

The plots shown in Fig. 4 are approximately linear up to $x_{\text{probe}} = 0.25$; the deviations from linearity at $x_{\text{probe}} = 0.30$ have also been observed in earlier probe experiments and may be due to a cooperative effect that partially counters the influence of the atropisomeric dopant.²² If the data points at $x_{\text{probe}} = 0.30$ are excluded, the results in Fig. 4a show that the polarization power of **MDW950** decreases by ca. 35% in the presence of either (+)-**1** or (–)-**1** (the two δ_p values are statistically identical), which suggests that dopant **1** exerts a perturbation on surrounding probe–host molecules that is approximately achiral in nature. On the other hand, the results in Fig. 4b show that the polarization power of **MDW950** decreases by 30% in the presence of (+)-**2**, but *increases* by 55% in the presence of (–)-**2**, which suggests that dopant **2** exerts a significant chiral perturbation on surrounding probe–host molecules. It is likely that the deviations in Fig. 4b include an achiral host effect contribution as the “host” composition changes from pure phenylpyrimidine to ca. 70 : 30 phenylpyrimidine–phenylpyridine.²⁸ However, an achiral host effect would shift both plots towards greater or smaller $|P_o|$ values and should not alter the non-superposable relationship of the two plots.

In the second series of probe experiments (Fig. 5), the polarization measurements reflect the combined effects of the homochiral atropisomeric dopant on each enantiomer of the probe. In the absence of any perturbation, or if the atropisomeric dopant exerts an achiral perturbation on the probe, the polarization is expected to be invariant with x_{rac} as the polarization induced by the (*R,R*) enantiomer of the probe should always be equal but opposite to that induced by the (*S,S*) enantiomer of the probe. In all other cases, the polarization is expected to vary with x_{rac} due to differences in the degree of chiral perturbation exerted by the homochiral dopant on each enantiomer of the probe, and/or to an achiral host effect on the homochiral dopant. The P_o vs. x_{rac} plots obtained with (+)-**1** and (–)-**1** show relatively small variations in P_o compared to the plots obtained with (+)-**2** and (–)-**2**, which is consistent with the results obtained in the first series of probe experiments.

Conclusions

In principle, the difference in $\delta_{p(\text{norm})}$ between dopants **1** and **2** may be explained by invoking either the Boulder model or the CTF model. In one case, the dopant behaves as a passive guest in a binding site that is approximately achiral. In the other case, the dopant behaves as an active guest and perturbs the achiral binding site through core–core interactions with surrounding host molecules. These interactions are assumed to be primarily chiral in nature, thus resulting in a chiral distortion of the binding site topography which leads to a feedback response by the chiral dopant. This feedback response may take the form of a shift in rotational distribution of the core transverse dipole moment and/or a change in polar ordering of the dopant. In the present study, the evidence suggests that the difference in

$\delta_{p(\text{norm})}$ may be due primarily to a greater propensity of dopant **2** to be an active guest by virtue of the helical topography of its atropisomeric core and the favorable structural match with the phenylpyrimidine core of the host to undergo chirality transfer *via* core–core interactions. It is important to note that the Boulder and CTF models are not mutually exclusive. In fact, the achiral binding site of the Boulder model may be viewed as one limit of a continuum over which the binding site is asymmetrically distorted to various degrees. In the present case, the dopant–host combination **2–PhP1** appears to lie significantly farther from the achiral end of the CTF continuum than **1–PhP1**.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on Bruker AC 200 and Avance 400 spectrometers in deuterated chloroform. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low resolution EI and ES mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer; peaks being reported as m/z (% intensity relative to the base peak). High resolution EI mass spectra were performed by the University of Ottawa Regional Mass Spectrometry Center. Polarized microscopy was performed using either a Nikon Eclipse E600 POL or Labophot-2 POL polarized microscope fitted with a Linkam LTS 350 hot stage. Melting points were determined on a Mel-Temp II melting point apparatus and are uncorrected.

Materials

All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled from Na–benzophenone under nitrogen. Flash chromatography was performed with 40–63 μm (230–400 mesh) silica gel (Silicycle). (*S,S*)- and (*R,R*)-5-(2,3-Difluorooctyl)-2-(4-octylphenyl)pyridine (**MDW950** and **MDW1290**, respectively) were supplied by Displaytech, Inc. (Longmont, Colorado). (+)- and (–)-2,2'-dimethyl-6,6'-dinitro-4,4'-bis[(4-*n*-nonyloxy)benzoyloxy]biphenyl ((+)-**1** and (–)-**1**) and (\pm)-2,2'-bis(bromomethyl)-4,4'-dihydroxy-6,6'-dinitrobiphenyl (**4**) were prepared according to published procedures and shown to have the expected physical and spectral properties.⁶

(\pm)-5,7-Dihydro-3,9-dihydroxy-1,11-dinitrodibenz[*c,e*]thiopin (**5**)

A solution of **4** (300 mg, 0.65 mmol) and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (470 mg, 1.95 mmol) in 10 : 1 MeOH– H_2O (110 mL) was refluxed under N_2 for 2 days. The mixture was diluted with 2 M aq. HCl (20 mL) and extracted with ether (3 \times 50 mL). The combined extracts were washed with H_2O , brine, dried (MgSO_4) and concentrated to a crude solid. Purification by flash chromatography on silica gel (80% EtOAc–hexanes) gave 183 mg (83%) of **5** as a yellow solid: mp 150–153 $^\circ\text{C}$; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 3.03 (d, $J = 12$ Hz, 2H), 3.66 (d, $J = 12$ Hz, 2H), 7.20 (d, $J = 2$ Hz, 2H), 7.41 (d, $J = 2$ Hz, 2H), 10.63 (s, 2H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 30.4, 110.4, 119.3, 120.3, 138.9, 147.8, 158.1; MS (EI) m/z 334 (M^+ , 8), 288 (5), 258 (53), 241 (19), 225 (14), 213 (7), 197 (13), 184 (6), 171 (11), 168 (9), 152 (12), 139 (20), 127 (9), 115 (26); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_6\text{S}$: 334.0259. Found: 334.0260.

(+)- and (–)-3,9-Bis[(4-nonyloxy)benzoyloxy]-5,7-dihydro-1,11-dinitrodibenz[*c,e*]thiopin ((+)-**2** and (–)-**2**)

A solution of 4-nonyloxybenzoic acid (40 mg, 0.15 mmol) and SOCl_2 (1 mL) in benzene (10 mL) was stirred at room temperature overnight under N_2 . The solution was then

concentrated and the residue dissolved in dry THF (20 mL). To this solution were added **5** (17 mg, 0.05 mmol) and DMAP (18 mg, 0.15 mmol) dissolved in dry THF (5 mL). The solution was stirred at room temperature overnight under N_2 , then diluted in ether (50 mL) and washed with 5% aq. NaOH, brine, dried (MgSO_4) and concentrated. The crude product was purified by flash chromatography on silica gel (CH_2Cl_2) to give 15.5 mg (40%) of (\pm)-**2** as a light yellow solid. The product was resolved by chiral phase HPLC using a Regis (*S,S*)-Whelk-O1 column (8 : 2 hexanes–isopropyl alcohol, 3 mL min^{-1}) to give (+)-**2** and (–)-**2** in optically pure forms. The resolved materials were recrystallized from hexanes prior to doping in **PhP1**: mp 130–132 $^\circ\text{C}$ (racemic); $[\alpha]_{\text{D}} = 60^\circ$ (c 0.75, CHCl_3); ^1H NMR (200 MHz, CDCl_3) δ 0.87 (t, $J = 7$ Hz, 6H), 1.27–1.50 (m, 24H), 1.75–1.88 (m, 4H), 3.32 (d, $J = 13$ Hz, 2H), 3.51 (d, $J = 13$ Hz, 2H), 4.05 (t, $J = 6$ Hz, 4H), 6.98 (d, $J = 9$ Hz, 4H), 7.60 (d, $J = 2$ Hz, 2H), 8.06 (d, $J = 2$ Hz, 2H), 8.13 (d, $J = 9$ Hz, 4H); ^{13}C NMR (50 MHz, CDCl_3) δ 14.1, 22.6, 26.0, 29.0, 29.2, 29.3, 29.5, 31.8, 68.4, 114.6, 118.0, 120.2, 126.0, 126.8, 132.5, 138.2, 147.7, 151.8, 163.8, 164.1; MS (electrospray) m/z 849 ($\text{M} + \text{Na}^+$), 865 ($\text{M} + \text{K}^+$).

Ferroelectric polarization and helical pitch measurements

Spontaneous polarizations (P_S) were measured as a function of temperature by the triangular wave method¹⁸ (6 V μm^{-1} , 80–100 Hz) using a Displaytech APT-III polarization testbed in conjunction with the Linkam LTS 350 hot stage. Polyimide-coated ITO glass cells (4 $\mu\text{m} \times 0.25 \text{ cm}^2$) supplied by Displaytech Inc. were used for all the measurements. 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.²³ Measurements of SmC* helical pitch (p) were carried out at $T - T_C = -10$ K on 150–225 μm films of the liquid crystal material in a planar alignment using polarized microscopy. The helical pitch was measured as the distance between dark fringes caused by the periodicity of the SmC* helix.²⁹

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$$\delta_p = \left(\frac{dP_o(x_d)}{dx_d} \right)_{x_d \rightarrow 0} \quad (2)$$

where x_d is the dopant mole fraction and P_o is the reduced polarization of the SmC* phase. K. Siemensmeyer and H. Stegemeyer, *Chem. Phys. Lett.*, 1988, **148**, 409. The reduced polarization is normalized for variations in tilt angle θ and is equal to $P_S/\sin \theta$. W. Kuczynski and H. Stegemeyer, *Chem. Phys. Lett.*, 1980, **70**, 123.

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