Chiral induction in nematic and smectic C liquid crystal phases by dopants with axially chiral 1,11-dimethyl-5,7-dihydrodibenz[e,c]thiepin cores†

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Three calamitic molecules with axially chiral cores, \((S)-3,9\text{-bis\{4-dodecyl\text{oxy}benzoyl\}\text{oxy}-1,11\text{-dimethyl-5,7-dihydrodibenz\text{e,c}\text{thiepin}\}}(5a), (R)-3,9\text{-bis\{4-butoxy\text{benzoyl}\}\text{oxy}-1,11\text{-dimethyl-5,7-dihydrodibenz\text{e,c}\text{thiepin}\}}(5b),\text{ and (R)-3,9\text{-bis\{4-octyloxy\text{benzoyl}\}\text{oxy}-1,11\text{-dimethyl-5,7-dihydrodibenz\text{e,c}\text{thiepin}\}}(5c)\text{, were synthesized in optically pure form and doped in four calamitic liquid crystal hosts with 1-N-SmA-SmC (INAC) phase sequences (PhP, PhB, NCB76 and DFT), and in the nematic host 5CB. Helical twisting powers (\(\beta\)) in the N* phase are in the range of 24–43 \(\text{mm}\text{c}^{-1}\) with the INAC hosts, and in the range of 56–58 \(\text{mm}\text{c}^{-1}\) with 5CB at \(T-T_{N-I}\) = –2 K, which are comparable to those previously reported for axially chiral binaphthyls. Interestingly, these dopants were found to stabilize and broaden the temperature range of the N* phase in 5CB. With some of the dopant-INAC host mixtures, the induction of a chiral TGB_{A*} phase was also observed. Dopant 5a induces a measurable spontaneous polarization in the SmC phase of the achiral phenylpyrimidine host PhP, giving a polarization power \(\delta_p\) of \(-104 \pm 20\ \text{nC cm}^{-2}\). Comparisons of helical twisting powers in the N* and SmC* phases, and polarization powers in the SmC* phase, for dopants 5a–c and the dinitro analogue (+)-1,11-dinitro-3,9-bis\{4-nonyloxybenzoyl\}\text{oxy}-5,7-dihydrodibenz\text{e,c\text{thiepin}}(4) suggest that the nitro substituents play a dominant role in promoting chirality transfer in the SmC* phase, whereas the helical topography of the core appears to be a more important factor in promoting chirality transfer in the N* phase.

Introduction

A common use of dopants in liquid crystal phases formed by rod-like (calamitic) molecules is the induction of chiral bulk properties such as the helical pitch of a chiral nematic phase (N*), also referred to as cholesteric or the spontaneous polarization of a chiral smectic C phase (SmC*).\(^1\)–\(^3\) The nematic phase is a fluid characterized by short-range orientational order of molecular long axes along a director \(n\); in the presence of a chiral dopant, the director \(n\) describes a helix that propagates along an axis perpendicular to \(n\), with a pitch that scales with the mole fraction of the dopant \(x_d\) and its enantiomeric excess ee. The propensity of a chiral dopant to induce a helical pitch \(p_N\) in a N* phase is expressed by the helical twisting power \(\beta\) according to eqn (1):

\[
\beta = (p_N x_d \text{ ee})^{-1}
\]

Despite the lack of translational order in the nematic phase, the magnitude of \(\beta\) often depends on a structural complementarity between chiral dopant and nematic host to achieve chirality transfer.\(^1\)–\(^4\) Gottarelli et al. were the first to show a correlation between the helical sense of induced cholesteric phases and the helicity of rigid atropisomeric dopants such as the bridged binaphthyl 1.\(^6\) They also showed that \(\beta\) values were highest in nematic hosts with core structures that were similar to the dopant (e.g., 1 in 5CB, \(\beta = 80 \text{ mm}\text{c}^{-1}\)), and lowest in nematic hosts that were structurally dissimilar (e.g., 1 in MBBA, \(\beta = 56 \text{ mm}\text{c}^{-1}\)).

These observations are consistent with a chiral perturbation model in which the handedness of the dopant is transferred to the ‘racemic’ host via chiral conformational interactions, as shown in Fig. 1. The term racemic is used in this context to reflect the fact that molecules like 5CB are chiral in the ground

![Fig. 1 Chiral conformational interactions between the binaphthyl dopant 1 and the liquid crystal host 5CB according to Gottarelli et al.](image)

Fig. 1 Chiral conformational interactions between the binaphthyl dopant 1 and the liquid crystal host 5CB according to Gottarelli et al.\(^6\)
state, but rapidly interconvert between enantiomeric conformations in the mesogenic temperature range. The chiral perturbation exerted by the dopant is then propagated throughout the host via similar conformational interactions between host molecules.

The host–guest molecular recognition postulated in the induction of chiral nematic phases may also be invoked in the induction of chiral smectic phases. In smectic phases, calamitic molecules are arranged in diffuse layers and exhibit short-range orientational and translational order. In the SmC phase, the director $n$ is uniformly tilted at a temperature-dependent angle $\theta$ with respect to the layer normal $z$, and rigid aromatic cores and flexible paraffinic side chains are segregated from one another, on the time average, which enables some degree of molecular recognition that discriminates between these two segments. In the chiral SmC* phase, the director $n$ precesses about $z$ in the absence of strong boundary conditions to form a helical structure with a pitch $p_C$. Another chiral bulk property of the SmC* phase is a spontaneous electric polarization $P_S$ oriented along the $C_2$ symmetry axis (polar axis) of each smectic layer. The magnitude of $P_S$ is a function of the structure and proportion of the chiral component(s) of the SmC* phase, and it can be negative or positive depending on the absolute configuration of the chiral component(s). As shown in Fig. 2, the SmC* phase in its helical form is not polar as the $P_S$ vectors add up to zero over one helical pitch. However, Clark and Lagerwall showed that the helical SmC* phase unwinds between rubbed polyimide-coated glass slides with a spacing on the order of the pitch (typically 1–5 $\mu$m) to give a surface-stabilized ferroelectric liquid crystal (SSFLC) with a net spontaneous polarization perpendicular to the plane of the glass slides. This polarization can be coupled to an electric field applied across the SSFLC film to produce an ON–OFF light shutter between crossed polarizers with a switching time on the order of microseconds. Ferroelectric liquid crystals are currently used in high-resolution reflective liquid-crystal-on-silicon (LCOS) microdisplays, and have potential applications in nonlinear optics, chiral sensing and photonics devices.

Commercial FLC mixtures are normally formed by mixing a chiral dopant in an achiral liquid crystal host mixture with low viscosity and broad temperature range in the SmC phase. The performance characteristics of FLC devices often depend on the magnitude of $P_S$ induced by the chiral dopant and, therefore, a key aspect of FLC materials research is to understand the relationship between the molecular structure of the chiral dopant and the magnitude of the polarization it induces. Stegemeyer and co-workers showed that this structure–property relationship can be expressed in terms of the polarization power $\delta_p$ according to eqn (2), where $x_d$ is the mole fraction of chiral dopant and $P_o$ is the polarization normalized for variations in tilt angle $\theta$ according to eqn (3).

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

$$P_o = P_S \sin \theta$$

At the molecular level, the origins of $P_S$ in the SmC* phase can be understood in terms of the rotational order about the director $n$ imposed on a chiral dopant by the achiral liquid crystal host, together with the asymmetric conformational distribution of any polar functional group that is coupled to one or more stereogenic center(s), which results in an orientational bias of molecular dipoles along the polar axis. Empirical and semiempirical structure–property relationships based on conformational analyses of such ‘stereo-polar units’ are well established for dopants with chiral side chains, which represent the vast majority of chiral dopants found in SmC* formulations, and the polarization power of these compounds is generally invariant with respect to the structure of the liquid crystal host.

Less conventional dopants with chiral cores induce spontaneous polarizations that tend to vary significantly with the structure of the liquid crystal host. This host effect may be viewed as a manifestation of molecular recognition via core–core interactions with the host molecules that 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. For example, we have shown that chiral dopants such as exhibit remarkably high polarization powers—up to 1738 nC cm$^{-2}$—in liquid crystal hosts with phenylpyrimidine cores, in which the atropisomeric core of the dopant can effectively transfer its chirality to surrounding host molecules via conformational interactions similar to those postulated by Gottarelli and Solliède in induced N* phases. The resulting chiral perturbations on the host are thought to cause a shift in the conformational distribution of the dopant that may enhance the induced polarization as a feedback effect (chirality transfer feedback, CTF). Early experimental evidence supporting this model include an inverse correlation between the helical pitch $p_C$ of the induced SmC* phase at a fixed dopant mole fraction ($x_d = 0.02$) and the polarization power $\delta_p$ for a series of dopants with varying side-chain length $n$.

A subsequent study focused on the influence of helical topography on $\delta_p$ by comparing the biphenyl dopant, in which the two aromatic rings form a dihedral angle of $90^\circ$, with the 5,7-dihydrodibenzo[c,e]thiepin dopant, in which the two aromatic rings form a dihedral angle of $64^\circ$ and describe a helical topography. We showed that the polarization power of the helical dopant is more than five times that of dopant in the phenylpyrimidine host PhP after normalizing for

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**Fig. 2** Schematic representation of the chiral SmC* phase in the absence of boundary conditions (left), and as a surface-stabilized ferroelectric liquid crystal film (right).
differences in core transverse dipole moment (99 vs. 19 nC cm$^{-2}$ D$^{-1}$, respectively), whereas the helical pitch $p_C$ induced by 4 at $x_d = 0.02$ is ca. five times shorter than that induced by $b_3$ (14 vs. 96 μm, respectively). These results suggest that the helical topography of 4 contributes to a higher $\delta_{\rho}$ by enhancing chirality transfer according to the CTF model, which is consistent with previous observations that $b_3$ values of atropisomeric biaryl dopants in cyanobiphenyl nematic hosts tend to be higher for bridged biaryls describing a rigid helical topography. However, a limitation of dopant 4 is its poor compatibility with the SmC phase of $\text{PhP}$, which precluded the investigation of chiral perturbations at dopant mole fractions greater than 0.05, including the observation of any cooperative effect. Solladie and co-workers previously reported that the optically pure 5,7-dihydrodibenz[c,e]thiepin ($R$)-5a, with methyl substituents instead of nitro substituents at C-1 and C-11, forms enantiotropic SmC* and N* liquid crystal phases (Cr 71 SmC* 90 N* 106 I). With the anticipation that such mesomorphic character would enable the study of chiral perturbations in $\text{PhP}$ over a much broader mole fraction range, we undertook the synthesis and characterization of compounds ($S$)-5a, ($R$)-5b and ($R$)-5c in optically pure form following a modification of the synthetic approach used to prepare compound 4. In this paper, we report that, contrary to the published account of Solladie et al., ($S$)-5a is not mesomorphic, but does induce a measurable polarization in $\text{PhP}$ over a broader mole fraction range than 4. Furthermore, a comparison of helical pitch measurements made in N* and SmC* phases induced by 5a–c and by the nitro-substituted analogues 2 and 4 suggests that the nitro substituents play a dominant role in promoting chirality transfer in the SmC* phase, whereas the helical topography of the core appears to be a more important factor in promoting chirality transfer in the N* phase.

### Results and discussion

#### Synthesis and characterization

As shown in Scheme 1, the synthesis of 5a–e began with commercial 2-nitro-3-methylbenzoic acid (6), which was converted to the racemic dimethyl biphenyldicarboxylate ($RS$)-7 in seven steps according to the procedure of Montoya-Pelaez and co-workers. Hydrolysis to the biphenyldicarboxylic acid ($RS$)-8 was followed by selective reduction to the diol ($RS$)-9 with BH$_3$·THF and then conversion to the dibromide ($RS$)-10 with CBr$_4$ and Ph$_3$P. The sulfide bridge was formed by treatment of the dibromide with Na$_2$S·9H$_2$O to give ($RS$)-11, which was reduced to the diamine ($RS$)-12 using SnCl$_2$·2H$_2$O. Hydrolysis of the corresponding bis-diazonium salt gave the diol ($RS$)-13, which was resolved on a preparative scale by chiral phase HPLC using a Daicel Chiralpak AS column to give ($R$)-13 and ($S$)-13 in 99% and 86% ee, respectively. The ($S$) enantiomer of 13 was also obtained in 95% ee by classical resolution of the diacid precursor ($RS$)-8 using quinine according to the procedure of Williams. The final compounds ($S$)-5a, ($R$)-5b and ($R$)-5c were obtained by esterification of the optically pure diols with the appropriate 4-alkoxybenzoic acids in 46–65% yields using DCC and DMAP.

![Scheme 1](attachment:scheme1.png)  
**Scheme 1** Reagents and conditions: (a) 0.5 M aq NaOH–EtOH (1 : 1), reflux, 94%; (b) BH$_3$·THF, 0°C, 74%; (c) CBr$_4$, Ph$_3$P, CH$_2$Cl$_2$, 78%; (d) Na$_2$S·9H$_2$O, EtOH; (e) SnCl$_2$·2H$_2$O, EtOH, 58%; (f) NaNO$_2$, 10% aq H$_2$SO$_4$, 0°C, then reflux, 79%; (g) preparative chiral phase HPLC resolution, 50 cm × 5 cm i.d. Chiralpak AS column, 90 : 10 hexanes–EtOH, 50 mL min$^{-1}$. This journal is © The Royal Society of Chemistry 2007
match those reported by Solladié et al. for \((R)-5a\), and
the specific rotation of our sample, \([\alpha]_D = +99\) (c = 0.02,
acetone), is consistent with, but does not match exactly, the
value reported for \((R)-5a\), \([\alpha]_D = -74\) (c = 2, acetone).30

Differential scanning calorimetric analysis of \((S)-5a\) (see ESI†) showed two phase transitions on heating with compar-
able enthalpies of transitions, one at 79 °C (\(\Delta H = 21.4\) kJ mol\(^{-1}\)) and another at 113 °C (\(\Delta H = 19.1\) kJ mol\(^{-1}\)), which are inconsistent with the phase transition temperatures reported by Solladié et al. for \((R)-5a\), and suggest the occurrence of a crystal–crystal transition instead of a crystal–
smectic phase transition. The texture change observed by polarized optical microscopy is also inconsistent with a
crystal–smectic phase transition. As shown in Fig. 3, heating a
thin film of \((S)-5a\) past the first transition point results in a
disappearance of crystalline spherulite patterns to give a grainy
texture that lacks the features normally observed with SmC* phases, i.e., pseudohomotropic and broken fan domains with
periodic fringe patterns. Similar observations were made on
cooling the sample from isotropic liquid. Furthermore, a 4 \(\mu m\)
film of \((S)-5a\) between ITO glass slides showed no electro-
optical response to an applied AC field of 6 V \(\mu m^{-1}\) in the
temperature range between the two phase transitions, on
heating or cooling, which rules out a ferroelectric SmC* phase.
Powder X-ray scattering profiles were recorded above and
below the first transition point. As shown in Fig. 4a, the profile
at 50 °C shows a series of sharp peaks at wide angle that are
consistent with a crystalline phase. These wide angle peaks persist past the first transition point, but their intensities and sharpness are attenuated (Fig. 4b), which suggests that the
higher temperature phase is a ‘softer’ crystalline phase and not
a diffuse lamellar mesophase like the SmC* phase. The DSC
profiles of the racemate \((RS)-5a\) and enantiomerically enriched
\((S)-5a\) (50% ee) showed single melting points on heating at 140
and 127 °C, respectively, with no evidence of monotropic
mesophase on cooling. The two derivatives with shorter side
chains, \((R)-5b\) and \(-5c\), also showed single melting points on
heating at 176 and 117 °C, respectively, with no monotropic
mesophase.

Dopant–host mixtures
The compatibilities of dopants \(5a–c\) with four different liquid
crystal hosts with I–N–SmA–SmC (INAC) phase sequences
(Fig. 5) were assessed by constructing phase diagrams (Fig. 6
and ESI†). Overall, the three dopants are more compatible with
these hosts than the dinitro analogue \(4\), and have relatively little effect on clearing points up to mole fractions
\(x_d\) of 0.20. In general, the doping of these compounds causes a
broadening of the N* and SmA* phases and a narrowing of
the SmC* phase, which may be caused by the greater lateral
steric demand of the axially chiral core relative to the cores of
host molecules.7 In addition, the appearance of a chiral twist

![Fig. 3 Polarized photomicrographs (100 ×) of (S)-5a at 25 °C (top) and at 95 °C (bottom) on heating.](image)

![Fig. 4 Powder X-ray scattering profiles of (S)-5a at (a) 50 °C and (b) 90 °C.](image)
The induction of a TGBA* phase by a chiral dopant is characteristic textures such as the filament texture in domains with homeotropic anchoring shown in Fig. 7a, and the spiral filament texture shown in Fig. 7b.33

The helical twisting power in the N* phase. Hence, we determined values were measured by the Grandjean method39 using commercial wedge cells (E.H.C.) and dopant-host mixtures with 0.01 \( \leq x_d \leq 0.05 \); the \( \beta \) values were obtained from the least-squares fits of \( p_{N}^{-1}(x_d) \) plots (see ESIF) according to eqn (1) and are listed in Table 1. The \( \beta \) values obtained for 5a–c are relatively high and compare favorably to those previously reported for axially chiral binaphthyls, which feature more extended helical topographies.40 This may be attributed in part to an increase in orientational order of the dopants in the N* phase due to their higher molecular anisometries.5 Indeed, the \( \beta \) values for 5a–c are high enough to achieve selective reflection in the visible range of the spectrum at mole fractions as low as 0.05. The \( \beta \) values are more or less invariant with respect to the length of the dopant side chains, or to the structure of the liquid crystal host.

To assess the influence of polar substituents and chiral topography on the helical twisting power of these dopants, we sought to compare the \( \beta \) value of (R)-5c in PhP with those of the helical dinitro dopant (+)-4 and the orthogonal 3,3’-dinitrophenyl dopant (R)-2b, which holds the highest ferroelectric polarization power in that host. We were unable to measure a \( \beta \) value for (+)-4 due to its destabilizing effect on the N phase of PhP, but did obtain a \( \beta \) value of 14 \( \mu \text{m}^{-1} \) for (R)-2b, which is less than half that obtained for (R)-5c. These results prompted us to measure \( \beta \) values in the room temperature nematogen 4-cyano-4’-pentylbiphenyl (5CB) over the mole fraction range 0.01 \( \leq x_d \leq 0.1 \). The results shown in Table 1 strongly suggest that the helical topography of the axially chiral core in 4 and 5 enhances chirality transfer in the N* phase compared to the axially chiral core of 2, in which the two phenyl rings are nearly orthogonal. Conversely, the data suggest that nitro substituents may have a negative effect on chirality transfer in the N* phase. Along with their high helical twisting powers in 5CB, an interesting property of dopants (R)-5b and (R)-5c is their effect on the clearing point \( T_{N-I} \). As shown in Fig. 8, \( T_{N-I} \) increases by 13 K upon doping (R)-5b in 5CB at \( x_d = 0.1 \), but decreases by 4 K upon doping the orthogonal (R)-2a at the same mole fraction. A similar effect was observed with (R)-5c.

### Ferroelectric polarization measurements

Homogeneous mixtures of (S)-5a in the four INAC liquid crystal hosts were prepared with 0.05 \( \leq x_d \leq 0.15 \). The mixtures were aligned as SSFLC films in rubbed polyimide-coated ITO glass cells with a spacing of 4 \( \pm \) 0.5 \( \mu \text{m} \) (E.H.C.) by slow cooling from the isotropic phase while applying a 100 Hz triangular wave AC field (6 V \( \mu \text{m}^{-1} \)) across the film. The spontaneous polarization \( P_S \) of each SSFLC film was measured at 5 K below the Curie point \( (T-T_C = -5 \text{ K}) \) by the triangular wave method,41 and the tilt angle \( \theta \) was measured by polarized microscopy as half the rotation between the two extinction positions corresponding to opposite polarization directions. The corresponding \( P_o \) values were calculated using eqn (3) and plotted as a function of \( x_d \) to give the polarization power \( \delta_p \) according to eqn (2). A linear \( P_o(x_d) \) plot was obtained for mixtures of (S)-5a in PhP (see ESIF), with a least-squares fit corresponding to a polarization power \( \delta_p \) of \(-104 \pm 20 \text{ nC cm}^{-2} \). However, the induced polarization in the other three hosts was below the detection limit of our instrument (ca. 0.3 nC cm\(^{-2} \)) with \( x_d \) as high as 0.15. No polarization could be measured for the shorter dopants (R)-5b and (R)-5c in any of the four hosts, which may be ascribed to a reduction in core–core correlation due to weaker anchoring of
Fig. 6  Phase diagrams for mixtures of dopant (S)-5a in the liquid crystal hosts (a) PhP, (b) NCB76, (c) PhB and (d) DFT.

Fig. 7  Polarized photomicrographs (100 ×) of TGBA* phases formed on cooling by (a) a 10 mol% mixture of (S)-5a in DFT at 75 °C and (b) a 15 mol% mixture of (R)-5c in PhB at 40 °C.
Table 1 Helical twisting powers $\beta$ in the liquid crystal hosts PhP, NCB76, PhB, DFT and 5CB measured at $T - T_{N-1} = -2$ K

<table>
<thead>
<tr>
<th>Dopant</th>
<th>$n$</th>
<th>PhP</th>
<th>NCB76</th>
<th>PhB</th>
<th>DFT</th>
<th>5CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S)-5a</td>
<td>12</td>
<td>$34 \pm 1$</td>
<td>$24 \pm 5$</td>
<td>$29 \pm 2$</td>
<td>$38 \pm 7$</td>
<td>$32 \pm 8$</td>
</tr>
<tr>
<td>(R)-5b</td>
<td>4</td>
<td>$43 \pm 7$</td>
<td>$38 \pm 2$</td>
<td>$28 \pm 4$</td>
<td>$24 \pm 1$</td>
<td>$58 \pm 4$</td>
</tr>
<tr>
<td>(R)-5c</td>
<td>8</td>
<td>$33 \pm 2$</td>
<td>$36 \pm 7$</td>
<td>$30 \pm 1$</td>
<td>$56 \pm 4$</td>
<td></td>
</tr>
<tr>
<td>(R)-2a</td>
<td>4</td>
<td>$7 \pm 1$</td>
<td>$6 \pm 1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(R)-2b</td>
<td>8</td>
<td>$14 \pm 1$</td>
<td>$15 \pm 2$</td>
<td>$15 \pm 3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(+)-4</td>
<td>9</td>
<td>$35 \pm 9$</td>
<td>$36 \pm 1$</td>
<td>$37 \pm 2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Uncertainty is $\pm$ standard error of least-squares fits of $\rhoN^{-1}(x_d)$ plots. $^b$ No N* phase at $x_d > 0.01$. $^c$ Measured at $T - T_{N-1} = -1$ K. $^d$ Based on a single pitch measurement.

Fig. 8 Clearing point $T_{N-1}$ as a function of dopant mole fraction $x_d$ for mixtures of (R)-5b (squares) and (R)-2a (circles) in 5CB.

We attempted to measure the helical pitch $p_C$ of the SmC* phase induced by (S)-5a and (R)-5b in PhP ($x_d = 0.02$, $T - T_C = -10$ K) using homemade cells with planar alignment conditions and spacings of 225 $\mu$m. However, the focal conic domains observed by polarized microscopy showed no periodic fringe pattern, as shown in Fig. 9, which indicates that the helical pitch of the induced SmC* pitch is $>200$ $\mu$m. By contrast, the pitch induced by (+)-4 in PhP under the same conditions is 14 $\mu$m.

Fig. 9 Photomicrographs of 2 mol% mixtures of (S)-5a in PhP (top) and (R)-5b in PhP (bottom) at $T - T_C = -10$ K as films confined to homemade cells with planar alignment conditions and spacings of 225 $\mu$m.

the shorter side chains in the smectic layers, as previously observed with the series of dopants 2 with varying side-chain length $n$. The higher polarization power of (S)-5a in PhP is consistent with the $\delta_p$-host trends previously observed with other dopants featuring axially chiral biphenyl cores, but it is ca. four times smaller than the $\delta_p$ value reported for the dinitro derivative (+)-4 in PhP at $T - T_C = -5$ K (463 nC cm$^{-2}$), which is due in part to the difference in transverse dipole moment of the axially chiral cores (vide infra).

The polarization powers were normalized by dividing each $\delta_p$ value by the transverse dipole moment $\mu_\perp$ of the corresponding 5,7-dihydrodibenz[c,e]thiepin core (14), which was calculated at the B3LYP/6-31G* level. The $\mu_\perp$ vectors of 14a and 14b lie along the C$_2$ symmetry axis of the cores, but are oriented in opposite directions. The exclusion of the ester linking groups in these calculations was justified by conformational analyses showing similar conformational energy profiles for rotation of the ester about the C–O single bond linking it to the core (see ESI†), which suggests that the transverse dipole moments of the ester linking groups in 4 and 5 make similar contributions to the polarization power. The normalized $\delta_p$ values of (+)-4 and (S)-5a are 99 and $-47$ nC cm$^{-2}$ D$^{-1}$, respectively, which suggests that the nitro groups in 4 play an important role in enhancing polar order. One could also account for this result by invoking a difference in rotational distribution of $\mu_\perp$ with respect to the polar axis. However, this may be ruled out by considering that the two cores have approximately the same degree of biaxiality, and their quadrupolar ordering in the SmC phase of the host PhP should therefore be more or less the same.21,22
Conclusions

The results of this study on dopants with axially chiral biaryl cores suggest that a core with helical topography is more effective at chirality transfer in the N* phase than a core in which the two aromatic rings are nearly orthogonal, which is consistent with previous observations made by Gottarelli and others. On the other hand, the introduction of nitro substituents at the C-1 and C-11 positions of the helical 5,7-dihydrodibenzo[c,e]thiepin core lowers the helical twisting power by ca. 40% in 5CB, which is inconsistent with a trend previously reported for a series of axially chiral 5,7-dihydrodibenzo[c,e]oxepins (15). In the latter case, the nitro substituents are thought to stabilize intermolecular arene–arene interactions that result in chirality transfer by reducing repulsive electrostatic forces and enhancing attractive dispersion forces. However, in the case of dopant 4, the nitro substituents are oriented differently with respect to the long axis of the dopant, which may alter how they interact with the host molecules and affect intermolecular interactions leading to chirality transfer in the N* phase.

![Diagram of 15]

In the induction of ferroelectric SmC* phases by dopants with axially chiral biaryl cores, we have previously shown that a helical topography improves the transfer of chirality by a core with lateral nitro substituents, and results in higher $\phi_p$ values. However, the results presented herein suggest that these lateral nitro substituents have a dominant, perhaps unique effect on chirality transfer in the SmC* phase, which correlates to significantly higher $\phi_p$ values after normalizing for differences in $\mu_L$. Indeed, it is possible that the difference in $\mu_{PC}$ induced by the orthogonal dinitro dopant 3 and helical dinitro dopant 4 in PHP could be attributed to the difference in asymmetric spatial relationship of the two nitro substituents with respect to the chiral axis, and not to the difference in helical topography of the biaryl cores themselves. The effect on $\phi_p$ notwithstanding, these results suggest that using helical twisting power in the N* phase as a guide to design chiral dopants for SSFLC formulation with improved CTF properties may not always be valid, especially in terms of substituent effects.

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