

# Molecular recognition in chiral smectic liquid crystals: The effect of core–core interactions and chirality transfer on polar order†

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This *critical review* focuses on the induction of polar order in smectic liquid crystal phases by dopants with axially chiral cores, and should be of interest to all practitioners of supramolecular chemistry. The variations in polarization power of these dopants with the core structure of the liquid crystal hosts is a manifestation of molecular recognition that reflects the nanosegregation of aromatic cores from paraffinic side-chains in smectic phases, and the collective effect of core–core interactions that enable the propagation of chiral perturbations. (76 references.)

## Introduction

Molecular recognition is defined as “the selective binding of a substrate by a molecular receptor to form a supramolecular species.”<sup>1</sup> Molecular recognition is ubiquitous in biological systems, and is at the basis of the various physiological responses elicited by highly specific host–guest interactions at the cellular level (*e.g.*, enzyme–substrate complexes, antibody–antigen, membrane receptors). The study of molecular recognition extends to increasingly diverse ‘artificial’ systems that are intended to mimic the host–guest interactions of biological systems; the vast majority of these studies have focused on host–guest systems with well defined architectures that are often described in the context of *supramolecular chemistry*.<sup>1,2</sup> In many natural and artificial systems, receptors consist of self-assembled supramolecular structures with unique functions or activities that are not found in the

molecular building blocks themselves. Such supramolecular structures rely on selective non-covalent interactions between complementary molecules, and may be composed of a finite number of molecular components,<sup>3</sup> or they may form ‘softer’ supramolecular functional materials such as liquid crystals.<sup>4</sup>

According to Lehn, “molecular recognition events represent the basis of information processing at the supramolecular level.”<sup>1</sup> In liquid crystal phases, the effect of a non-mesogenic guest (dopant) on the supramolecular (bulk) properties of a liquid crystal host often depends on molecular recognition to process *and* propagate the ‘information’ coded into the structure of the dopant. One of the most common uses 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\*).<sup>5–7</sup> 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* in a N\* phase is expressed by the helical twisting power  $\beta_M$  according to eqn (1):

$$\beta_M = (p x_d ee)^{-1} \quad (1)$$

Despite the lack of translational order in the nematic phase, the magnitude of  $\beta_M$  often depends on a structural complementarity between chiral dopant and nematic host to achieve *chirality transfer*.<sup>5,8,9</sup> Gottarelli and Solladié 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**.<sup>10</sup> They also showed that  $\beta_M$  values were highest in nematic hosts with core structures that were similar to the dopant (*e.g.*, **1** in **5CB**,  $\beta_M = +80 \mu\text{m}^{-1}$ ), and lowest in nematic hosts that were structurally dissimilar (*e.g.*, **1** in **MBBA**,  $\beta_M = +56 \mu\text{m}^{-1}$ ). Conversely, the helical twisting power of a chiral dopant such as the oxirane **2** was shown to be higher in **MBBA** ( $-42 \mu\text{m}^{-1}$ ) than in a mixture of cyanobiphenyls ( $-11 \mu\text{m}^{-1}$ ).<sup>11</sup>

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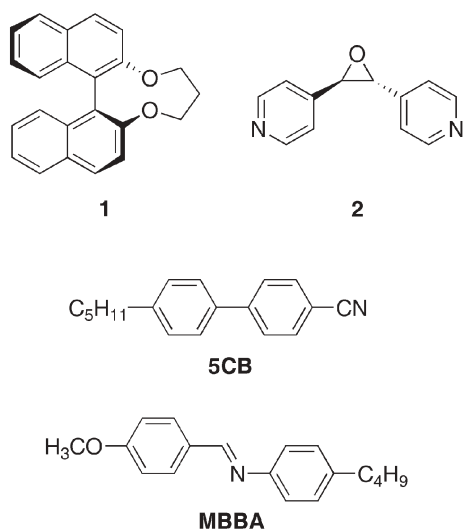
† In memory of Dr Michi Nakata



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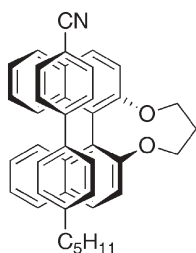
Bob Lemieux was born in Montréal, Québec in 1962. He received his BA from Colgate University in 1984 and his PhD in organic chemistry from the University of Illinois at Urbana-Champaign in 1989 under the direction of Peter Beak. He worked as a postdoctoral research associate at the University of Illinois under the direction of Gary Schuster from 1989 to 1992 and then joined the faculty at Queen's University, where he is presently Professor of Chemistry and Department Head. His research interests include the design of new materials for the induction and photomodulation of chiral bulk properties in liquid crystal phases, and the study of non-covalent interactions and self-assembly in liquid crystals and other soft materials.

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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 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. Such a manifestation of molecular recognition is also possible in chiral smectic liquid crystal phases. This review focuses on this phenomenon as it pertains to the induction of polar order in smectic liquid crystal phases by dopants with axially chiral cores.

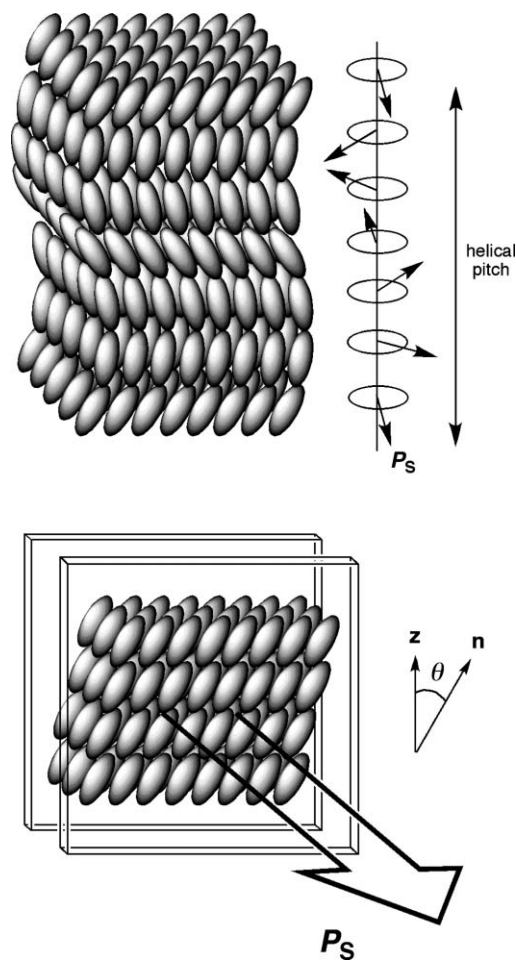
In smectic phases, calamitic molecules are arranged in diffuse layers and exhibit short-range orientational and translational order. In the smectic A (SmA) phase, molecular long axes are oriented along a director  $\mathbf{n}$  that is parallel to the layer normal  $\mathbf{z}$ ; in the smectic C (SmC) phase, the director  $\mathbf{n}$  is uniformly tilted at a temperature-dependent angle  $\theta$  with respect to  $\mathbf{z}$ . In the SmA and SmC phases, 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. Such *nanosegregation* can be further enhanced by increasing the amphiphilic character of calamitic molecules, including the modification of side-chains with oligosiloxane, perfluorinated or hydroxylic end-groups.<sup>4</sup>



**Fig. 1** Chiral conformational interactions between the binaphthyl dopant **1** and the liquid crystal host **5CB** according to Gottarelli *et al.*<sup>10</sup>

The chiral SmC\* phase forms a helical structure in which the director  $\mathbf{n}$  precesses about the layer normal  $\mathbf{z}$  in the absence of boundary conditions (Fig. 2). 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.<sup>12</sup> 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 left-handed (negative) or right-handed (positive) depending on the absolute configuration of the chiral component(s).<sup>13,14</sup> The sign of  $P_S$  is positive if it points in the same direction as the cross-product  $\mathbf{z} \times \mathbf{n}$  according to the physics convention.<sup>15</sup> 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  $\mu\text{m}$ ) to give a *surface-stabilized ferroelectric liquid crystal* (SSFLC) with a net spontaneous polarization perpendicular to the plane of the glass slides.<sup>16</sup>

A SSFLC can be switched from one tilt orientation to the other on a microsecond time scale by coupling the polarization



**Fig. 2** Schematic representation of the chiral SmC\* phase in the absence of boundary conditions (top), and as a surface-stabilized ferroelectric liquid crystal film (bottom). The sign of polarization shown in this figure is negative.

to an electric field  $E$  (Goldstone-mode switching) to produce a bistable ON/OFF light shutter between crossed polarized filters (Fig. 3). Ferroelectric liquid crystals are currently used in high-resolution reflective liquid-crystal-on-silicon (LCOS) microdisplays,<sup>17</sup> and have potential applications in nonlinear optics,<sup>18</sup> chiral sensing<sup>19</sup> and photonics devices.<sup>20–22</sup> Commercial FLC mixtures are normally formed by mixing a chiral dopant in an achiral SmC liquid crystal host mixture with low viscosity and wide temperature range. The performance characteristics of FLC devices, including the electro-optical switching time, second-order NLO susceptibility, enantiomeric enrichment detection limit and photoswitching threshold, depend in part on the magnitude of  $P_S$  induced by the chiral dopant. Consequently, a key aspect of FLC materials research is to understand the relationship between the molecular structure of a chiral dopant and the magnitude of the spontaneous polarization it induces (*vide infra*).<sup>7,13,23–25</sup> This structure–property relationship can be expressed in terms of the polarization power  $\delta_P$  according to eqn (2),<sup>26</sup> where  $P_o$  is the reduced polarization, which is normalized for differences in tilt angle  $\theta$  according to eqn (3).<sup>27</sup>

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

$$P_o = P_S / \sin \theta \quad (3)$$

The chiral SmA\* phase cannot be distinguished from the achiral SmA phase in the absence of external perturbation. However, Garoff and Meyer showed that an electric field  $E$  applied parallel to the layers of a SmA\* liquid crystal induces a tilt  $\theta$  with respect to  $z$  in a direction orthogonal to the field (Fig. 3).<sup>28</sup> This *electroclinic effect* is described by a phenomenological model derived from Landau theory which predicts a

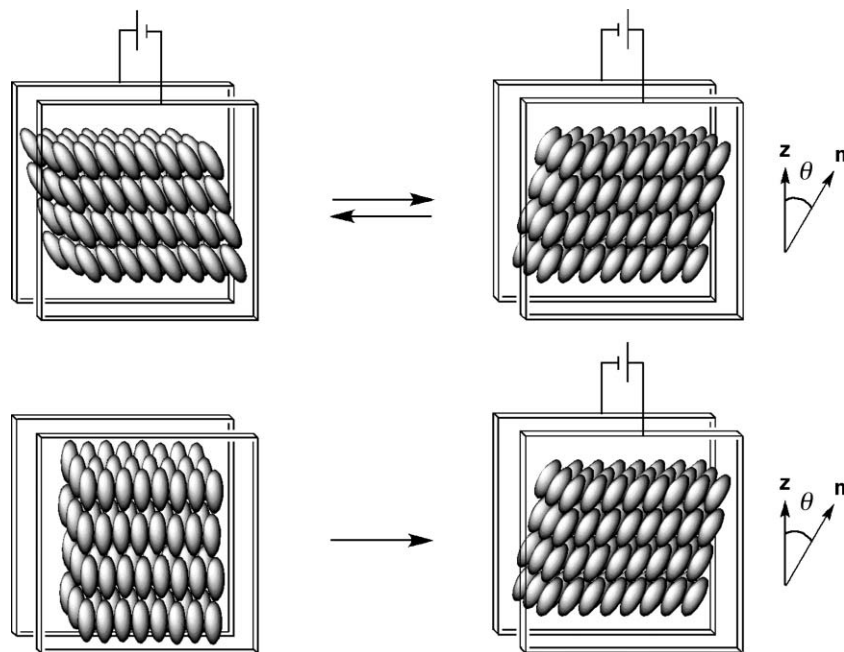
linear dependence of the induced tilt angle  $\theta$  on the applied field  $E$  at low field strengths.<sup>29</sup> This relationship is expressed by eqn (4) and (5),

$$\theta = e_c E \quad (4)$$

$$e_c = \frac{c}{\alpha(T - T_C)} \quad (5)$$

where  $e_c$  is the electroclinic coefficient,  $c$  is the electroclinic coupling constant, and  $\alpha(T - T_C)$  is the first coefficient of the Landau free-energy expansion. The term  $\alpha$  is a nonchiral parameter known as the tilt susceptibility coefficient, or tilt elastic modulus, which describes the restoring torque taking the director back to the layer normal. The term  $c$  is a chiral parameter describing the coupling between the spontaneous polarization and the tilt  $\theta$  in the SmC\* phase.<sup>30</sup> The relationship between  $\theta$  and  $E$  normally deviates from linearity at high field strengths and/or when the temperature approaches the Curie point  $T_C$  corresponding to the second-order transition from the tilted SmC\* to the orthogonal SmA\* phase.

The linear relationship between the induced electroclinic tilt and  $E$  at low field strengths makes it possible to generate a gray scale display between crossed polarizers, and its response time may be orders of magnitude faster than a SSFLC display.<sup>31</sup> Such properties make electroclinic SmA\* materials suitable for a wide range of electro-optical device applications, including micro-color filters, tunable color filters and spatial light modulators.<sup>32</sup> To develop electroclinic materials for device applications, several groups have focused their efforts on the design of chiral SmA\* liquid crystals with high electroclinic coefficients,<sup>33–37</sup> including de Vries SmA\* liquid crystals,<sup>38–46</sup> which are characterized by a tilted molecular orientation with random azimuthal distribution.<sup>47,48</sup> However,



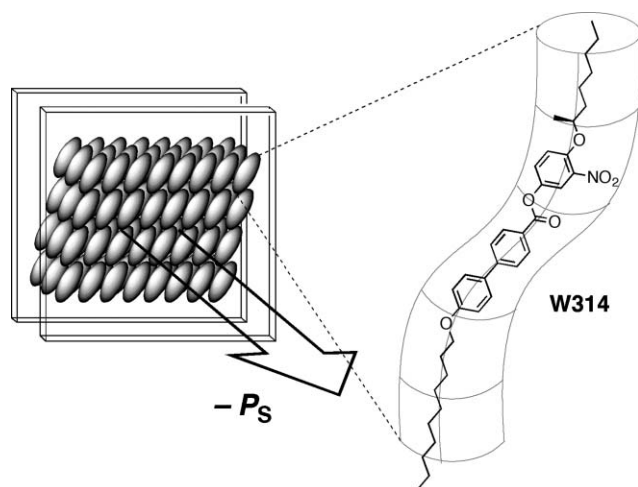
**Fig. 3** Goldstone-mode switching of a SSFLC with positive  $P_S$  (top), and electroclinic switching of a SmA\* liquid crystal in a planar alignment (bottom).

the design of SmA\* liquid crystals suitable for device applications is also a multi-variable problem that requires the optimization of achiral parameters unrelated to the electroclinic properties. To address this problem, one can apply the strategy used with commercial FLC mixtures and combine a chiral dopant that induces the desired electroclinic response at low concentration with an achiral SmA liquid crystal host mixture.<sup>49–51</sup> In general, SmA\* liquid crystals with large  $e_c$  values exhibit large spontaneous polarizations in the SmC\* phase. Hence, chiral dopants with large  $\delta_p$  values may be useful in formulating SmA\* liquid crystal mixtures for electroclinic device applications.

### Molecular origins of polar order in the SmC\* phase

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  $\mathbf{n}$  imposed on the chiral dopant by the achiral liquid crystal host, together with the asymmetric conformational energy profiles of polar functional groups which are coupled to the stereogenic center (stereo-polar coupling). According to the Boulder model, the SmC phase is considered to be a supramolecular host, and the ordering of a guest molecule is modeled by a mean-field potential which qualitatively behaves like a receptor or ‘binding site’ (Fig. 4). This binding site is  $C_{2h}$  symmetric and has a zigzag shape corresponding to a preferred rotational state in which the aromatic core is more tilted than the paraffinic side-chains, as deduced from comparisons of steric and optical tilt angles derived from small angle X-ray scattering measurements and polarized microscopic observations, respectively.<sup>52</sup>

When a chiral dopant is confined to this binding site, steric coupling between a polar functional group and the stereogenic center results in an orientational bias of the corresponding dipole moment along the polar axis that contributes to  $P_S$ . For example, Walba showed that SmC\* mesogens containing a chiral *o*-nitro-(2-octyloxy)phenyl unit, e.g., **W314**, exhibit high spontaneous polarizations due to steric coupling of the chiral alkoxy group to the polar *o*-nitrophenyl group, which forces



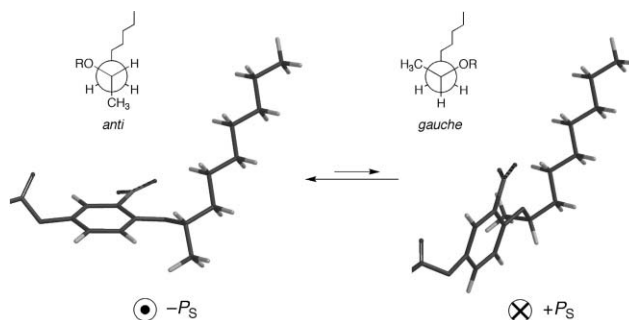
**Fig. 4** The SmC\* mesogen **W314** confined to the binding site of the Boulder model.

their transverse dipole moments in the same direction along the polar axis.<sup>53</sup> According to the Boulder model, the *stereo-polar unit* of **W314** can adopt two staggered conformations in which the coupled alkoxy/*o*-nitrophenyl dipoles are oriented along the polar axis (the third staggered conformation orients the dipoles in the tilt plane and cannot contribute to  $P_S$ ), as shown in Fig. 5.<sup>13</sup> These two conformations are non-equivalent, with the *anti* conformation being favored over the *gauche* conformation, which corresponds to a negative polarization in accordance with experimental observations.<sup>53</sup>

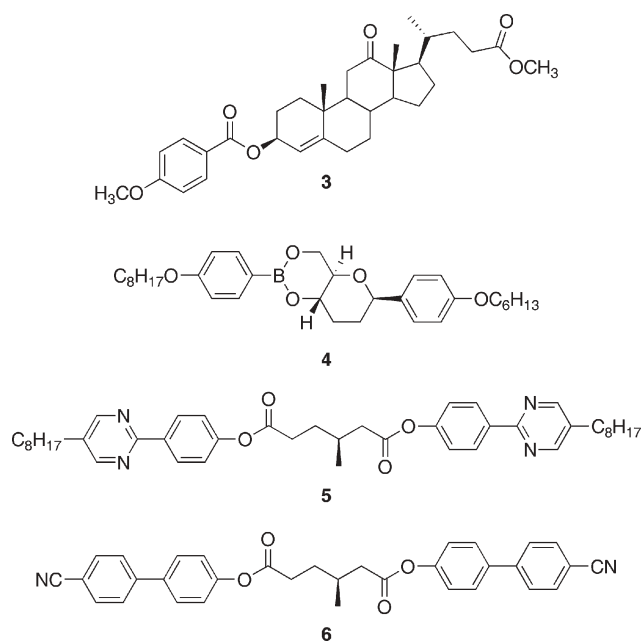
### Type I vs. Type II dopants

The vast majority of chiral dopants known to induce a ferroelectric SmC\* phase have stereo-polar units located in one of the side-chains and, in general, the polarization power of these dopants is more or less invariant of the achiral host structure. These were classified by Stegemeyer as ‘Type I’ dopants to distinguish them from dopants with stereo-polar units located in the rigid core (e.g., **3** and **4**), which were classified as ‘Type II’.<sup>54,55</sup> Stegemeyer was the first to show that the polarization power of a Type II dopant varies with the structure of the achiral host, which may be viewed as a manifestation of molecular recognition *via* core–core interactions with the host molecules that cannot be achieved with conventional Type I dopants due to the higher degree of conformational disorder among side-chains in the diffuse layer structure of the SmC phase. Another example of such molecular recognition was reported by Yoshizawa and Nishiyama who found that the twin dopant **5** induces a much shorter SmC\* helical pitch than the twin dopant **6** in a liquid crystal host with a phenylpyrimidine core, but approximately the same N\* helical pitch as **6**.<sup>56</sup> They ascribed this effect to the intercalation of chiral twin dopants between adjacent smectic layers and the difference in core–core interactions between dopant and host molecules, which affect the propagation of molecular chirality to the supramolecular assembly *via* interlayer correlation.

Stegemeyer explained the Type II host effect based on an extension of a microscopic model by Zeks,<sup>57</sup> which suggests that the spontaneous polarization induced by a Type II chiral dopant is influenced by steric interactions with the surrounding host molecules that affect the rotational distribution of the



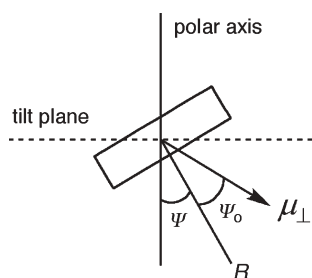
**Fig. 5** AM1-minimized conformations of the (*S*)-2-octyloxy side-chain of **W314** in the SmC\* phase according to the Boulder model, and as Newman projections about the C2–C3 bond. The direction of  $P_S$  conforms to the physics convention.



core transverse dipole moment  $\mu_{\perp}$  with respect to the polar axis of the SmC\* phase.<sup>54</sup> The spontaneous polarization is expressed as a function of  $\mu_{\perp}$  by eqn (6):

$$P_S = N_1 \mu_{\perp} \cos \psi_o \langle \cos \psi \rangle \quad (6)$$

where  $N_1$  is the dopant number density,  $\psi_o$  is the angle between  $\mu_{\perp}$  and a molecular reference axis  $R$  of the dopant and  $\langle \cos \psi \rangle$  is the polar order parameter, ranging from 0 to 1, that is related to the conformational asymmetry of the stereo-polar unit (Fig. 6). According to this model, the Type II host effect arises from variations in the rotational distribution of  $\mu_{\perp}$  ( $\cos \psi_o$ ) caused by rigid core-core interactions with surrounding host molecules. Hence, a chiral dopant with high polar order may yet induce a low polarization in one host if  $\mu_{\perp}$  is oriented near the tilt plane, and a high polarization in another host if  $\mu_{\perp}$  is oriented near the polar axis. This model is consistent with the Boulder model, and the assumption that a chiral dopant plays the role of a ‘passive’ guest which adopts a conformation and rotational distribution that best fits the shape of the binding site. In another microscopic model, Stegemeyer suggested that intermolecular chirality transfer could contribute to the Type II host effect by causing a polar

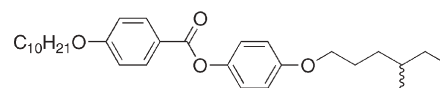


**Fig. 6** Schematic view of a Type II core along  $\mathbf{n}$ , showing the orientation of the molecular reference axis  $R$  and the transverse dipole moment  $\mu_{\perp}$  with respect to the polar axis and the tilt plane of the SmC\* phase.

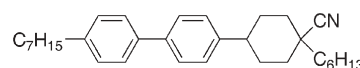
ordering of the host, thus inducing an additional polarization that scales with the transverse dipole moment of the host molecule.<sup>54</sup> In this case, the chiral dopant would be considered an ‘active’ guest perturbing its environment.

## Polarization power of axially chiral biphenyl dopants

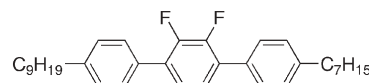
Only a few examples of axially chiral SmC\* mesogens are known, including allene, alkylidencyclohexane and 5,7-dihydrodibenzo[*c,e*]thiepin derivatives, and butadiene iron tricarbonyl complexes.<sup>58–61</sup> In all but one case, relatively small  $P_S$  values ranging from 12 to 38 nC cm<sup>-2</sup> were reported for the neat SmC\* liquid crystals; no  $P_S$  values were reported for the 5,7-dihydrodibenzo[*c,e*]thiepin derivatives.<sup>60</sup> The first example of a chiral dopant with an axially chiral biphenyl core reported to induce a ferroelectric SmC\* phase is the 2,2'-dinitro dopant **7a**,<sup>62</sup> which was followed by the 3,3'-dinitro dopant series **8a–i**.<sup>63</sup> The polarization powers of these dopants were measured in four liquid crystal hosts, all with I–N–SmA–SmC (INAC) phase sequences but with markedly different core structures (Fig. 7). The  $\delta_p$  values obtained for these compounds revealed some important trends. First,  $\delta_p$  values for the 2,2'-dinitro dopant **7a** are significantly smaller than those for the corresponding 3,3'-dinitro dopant **8d** (Fig. 8). This is consistent with a conformational analysis based on the Boulder model which suggests that the polarization induced by these compounds originates from a small bias in the energy profile for rotation of the core with respect to the two ester C–O bonds (Fig. 9). Calculations at the B3LYP/6-31G(d) level predict that the conformational bias should increase substantially when the symmetry-breaking nitro groups are moved from the 2-position to the 3-position, and that conformation **B** should be favored in the case of series **8a–i**.<sup>64,65</sup> According to this model, the (*R*) enantiomer of **8a–i** should induce a negative polarization. This was confirmed by a correlation of the sign of polarization induced by **8e** with the absolute



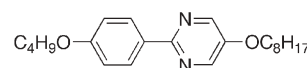
**PhB**; phase sequence: Cr 35 SmC 70.5 SmA 72 N 75 I



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

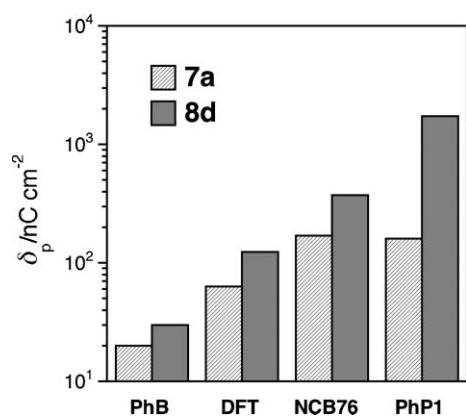


**DFT**; phase sequence: Cr 49 SmC 77 SmA 93 N 108 I

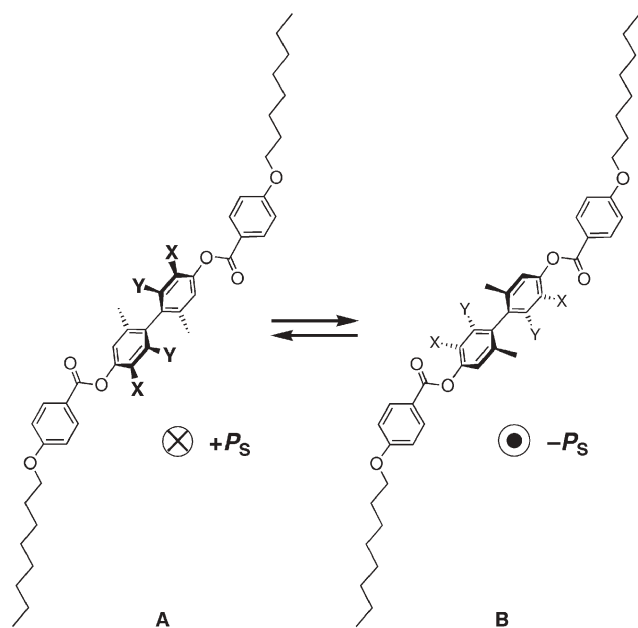


**PhP1**; phase sequence: Cr 58 SmC 85 SmA 95 N 98 I

**Fig. 7** Liquid crystal host structures and phase transition temperatures in °C.



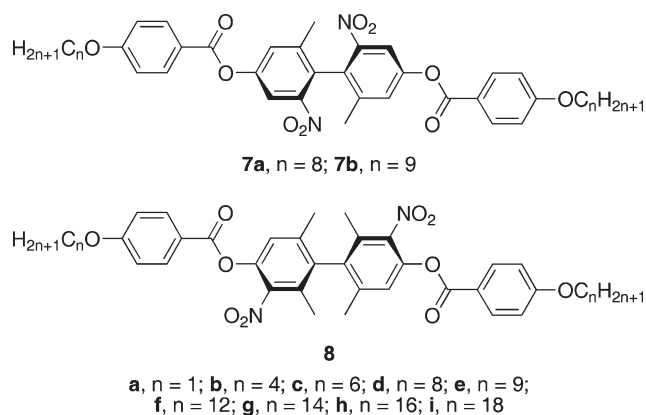
**Fig. 8** Absolute values of polarization power  $\delta_p$  for dopants **7a** and **8d** in the hosts **PhB**, **DFT**, **NCB76** and **PhP1** at 5 K below the Curie point ( $T - T_C = -5$  K).



**Fig. 9** Rotation of the biphenyl core about the two ester single bonds of dopants (*R*)-**7a** ( $X = \text{H}$ ,  $Y = \text{NO}_2$ ) and (*R*)-**8d** ( $X = \text{NO}_2$ ,  $Y = \text{Me}$ ) in a zigzag conformation consistent with the Boulder model. The direction of  $P_s$  conforms to the physics convention.

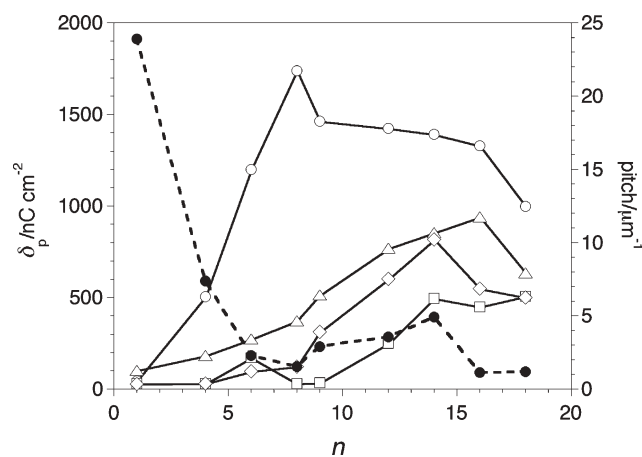
configuration of its biphenyl core, which was determined by X-ray crystallographic analysis of a bis-(1*S*)-10-camphorsulfonamide derivative.<sup>66</sup>

Secondly, the polarization power of these dopants strongly depends on the nature of the liquid crystal host, as predicted by Stegemeyer for Type II dopants, but on a much larger scale than reported heretofore. For example, the polarization power of **8d** in **PhB** is so small ( $< 30 \text{ nC cm}^{-2}$ ) that one cannot measure a polarization up to a mole fraction of 0.05;<sup>67</sup> on the other hand, its polarization power in **PhP1** ( $1738 \text{ nC cm}^{-2}$ ) is the highest reported thus far in the literature for a chiral dopant of any type. Third, the polarization power of **8a–i** varies with the length of the alkoxy side-chain  $n$  (Fig. 10). Because longer side-chains should increase the translational ordering of the dopant with respect to surrounding host

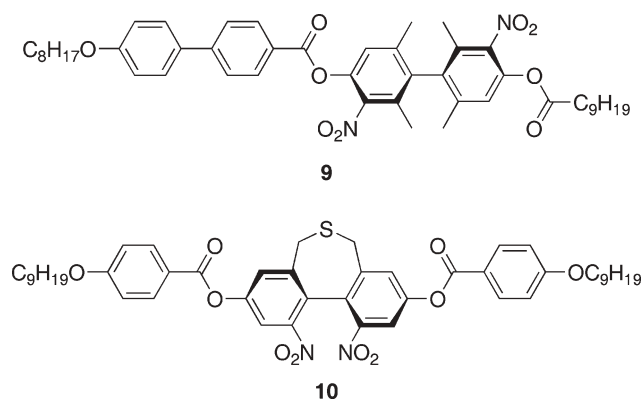


molecules, and therefore enhance the segregation of cores with respect to the side-chains, these results suggest that  $\delta_p$  is enhanced by core–core interactions between dopant and host molecules. The profiles shown in Fig. 10 suggest that the dependence of  $\delta_p$  on core–core interactions is more pronounced in the phenylpyrimidine liquid crystal host **PhP1**. An early test of this hypothesis was based on the unsymmetrical dopant **9**. This compound has approximately the same length as **8d**, but the position of the atropisomeric core is offset relative to the core sublayer of the SmC phase, which should reduce core–core interactions with surrounding host molecules on the time average. Measurements showed that the polarization power of **9** in **PhP1** is ca. 35% less than that of **8d** ( $1101$  vs.  $1738 \text{ nC cm}^{-2}$ , respectively), which is consistent with the postulated dependence of  $\delta_p$  on core–core interactions.

According to Stegemeyer, the host dependence of  $\delta_p$  may be ascribed (i) to a change in the rotational distribution of the core transverse dipole moment as the dopant ‘responds’ to a change in the topography of the binding site and/or (ii) to a transfer of chirality from dopant to host molecules, which causes a polar ordering of the latter. In the case of dopants **7** and **8**, it is noteworthy that the highest  $\delta_p$  values were obtained in the host that provides the best structural match for chirality transfer *via* chiral conformational interactions (**PhP1**), as



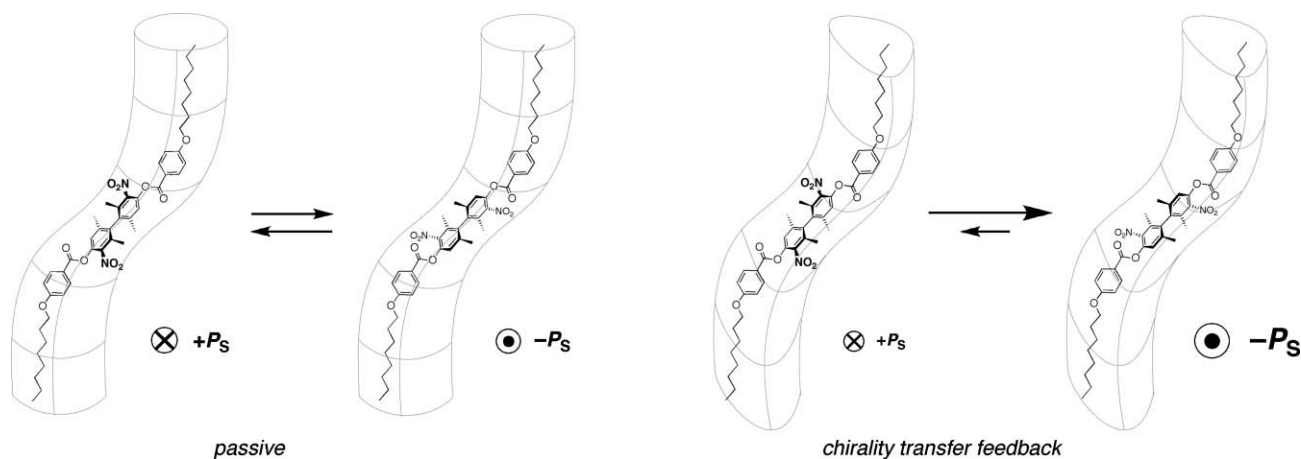
**Fig. 10** (a) Absolute values of polarization power  $\delta_p$  vs alkoxy chain length  $n$  for dopants **8a–i** in the hosts **PhB** ( $\square$ ), **DFT** ( $\diamond$ ), **NCB76** ( $\triangle$ ) and **PhP1** ( $\circ$ ) at 5 K below the Curie point ( $T - T_C = -5$  K). (b) SmC\* helical pitch vs  $n$  in the host **PhP1** at  $T - T_C = -10$  K with a dopant mole fraction  $x_d = 0.02$  ( $\bullet$ ).



originally proposed by Gottarelli and Solladié for chiral induction in nematic liquid crystals,<sup>10</sup> and the lowest  $\delta_p$  values in the host with the worst structural match for chirality transfer (**PhB**). In the  $\text{SmC}^*$  phase, the degree of chirality transfer may be correlated to the inverse helical pitch  $1/p$  in the absence of surface-stabilization (Fig. 2). In the host **PhP1**, we found that the pitch of the  $\text{SmC}^*$  phase induced by dopants **8a–i** varies with the alkoxy chain length  $n$  following a trend opposite to that observed for  $\delta_p$  vs  $n$  (Fig. 10), which suggests that chirality transfer may indeed play an important role in enhancing  $\delta_p$ .<sup>63</sup> This hypothesis was further supported by data obtained for the bridged biphenyl dopant **10**, which is similar to the 2,2-dinitro dopant **7b** in terms of its conformational distribution about the ester C–O bonds, but features a helical topography that should enhance chirality transfer *via* core–core interactions.<sup>65</sup> After normalizing for differences in transverse dipole moment, we found that the polarization power of **10** is about five times greater than that of **7b** (99 vs 19  $\text{nC cm}^{-2} \text{D}^{-1}$ , respectively), whereas the  $\text{SmC}^*$  pitch induced by **10** at  $x_d = 0.02$  is almost seven times shorter than that induced by **7b** (14 vs 96  $\mu\text{m}$ , respectively).

### Chirality Transfer Feedback model

The model for  $\delta_p$  amplification *via* chirality transfer proposed by Stegemeyer invokes a polar ordering of the liquid crystal host in which the host molecules effectively become chiral



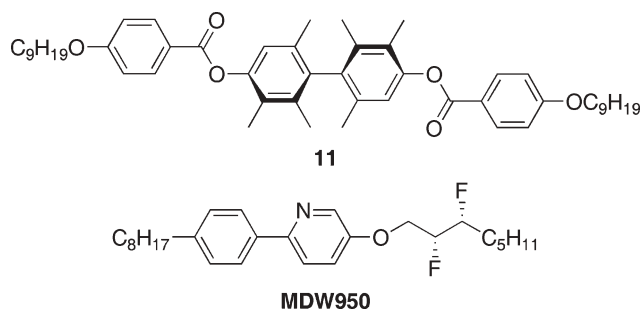
**Fig. 11** The effect of a chiral distortion of the binding site on the conformational equilibrium of dopant (*R*)-**8d** according to the Chirality Transfer Feedback model.

dopants and induce an additional polarization that should scale with their transverse dipole moment. However, considering that **PhP1** molecules are non-polar in the isotropic phase, and should only be weakly polar in a chiral  $\text{SmC}^*$  phase assuming that a chiral perturbation distorts the planar phenylpyrimidine core into a non-planar helical conformation, the unprecedented scale of  $\delta_p$  host dependence observed with dopants such as **8d** suggests that the effect of chirality transfer on the induced polarization may go beyond a polar ordering of the host. Alternatively, we proposed that chirality transfer could have a feedback effect on the polarization power of the dopant.<sup>7,63</sup> According to this ‘Chirality Transfer Feedback’ (CTF) model, a chiral perturbation of surrounding host molecules results in a chiral distortion of the binding site which, as a feedback effect, causes a shift in the conformational equilibrium of the chiral dopant favoring one orientation of the transverse dipole moment  $\mu_{\perp}$  along the polar axis (Fig. 11). The shift would occur by virtue of the diastereomeric relationship between ‘host–guest complexes’ formed by the 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 due to a shift in the rotational distribution of  $\mu_{\perp}$  with respect to the polar axis, in accordance with Stegemeyer’s other model.

The CTF model differs from conventional supramolecular chemistry concepts in the sense that a chiral perturbation of the host by the chiral guest has a feedback effect on the latter, which may be viewed as a dynamic form of chiral molecular imprinting.<sup>7,68</sup> Although the Boulder model assumes that the chiral dopant behaves as a passive guest in a binding site that is  $\text{C}_{2h}$ -symmetric, the CTF model may be viewed conceptually as an extension of the Boulder model that takes into account the active nature of dopants with topographically chiral cores.

### Probe experiments

A more direct assessment of the chiral perturbation exerted by a chiral biphenyl dopant on surrounding host molecules was first achieved using a host mixture consisting of **PhP1** and a ‘probe’ chiral dopant that mimics the structure of **PhP1**.<sup>65,69</sup>

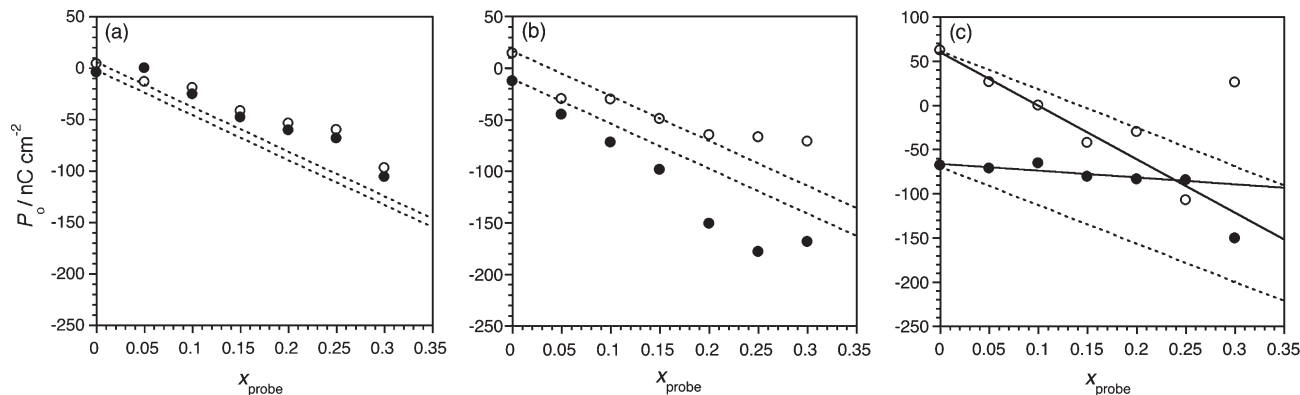


These probe experiments relied on the reasonable assumption that a perturbation exerted by a chiral biphenyl dopant on the probe/host mixture should cause a variation in the polarization power of the probe  $\delta_{\text{probe}}$  that scales with the magnitude of the perturbation. The Displaytech compound **MDW950** was selected as probe in **PhP1** due to its high compatibility with the latter, and the fact that its polarization power showed moderate Type II behavior in the four liquid crystal hosts in Fig. 7.<sup>70</sup> In the first part of these probe experiments, a reference plot was obtained by measuring the reduced polarization  $P_o$  (eqn (3)) of mixtures composed of **MDW950** and **PhP1** over the mole fraction range  $0 < x_{\text{probe}} \leq 0.30$  at  $T - T_C = -5$  K, which gave a good least-squares fit with a slope corresponding to a  $\delta_{\text{probe}}$  value of  $-435 \text{ nC cm}^{-2}$ . In the second part of each experiment, the  $P_o$  measurements were repeated in the presence of each enantiomer of the chiral biphenyl dopant at a constant mole fraction  $x_d = 0.04$ , and the resulting plots of  $P_o$  vs  $x_{\text{probe}}$  were compared to the reference plot (Fig. 12a–c). In each case, the reference plot is shifted along the  $y$ -axis by a value equal to  $P_o$  induced by the chiral biphenyl dopant in the absence of **MDW950** (shown as dashed lines), and represents the result expected if the polarizations induced by the chiral biphenyl and probe dopants are additive, *i.e.*, if the former is passive and does not perturb the probe/host mixture. On the other hand, if the chiral biphenyl dopant perturbs the probe/host mixture, a deviation from the reference plot should be observed due to the effect of the perturbation on the conformational and/or rotational distribution of the probe. Whether the perturbation is achiral or chiral in nature can be determined by comparing the plots obtained with each

enantiomer of the chiral biphenyl dopant. If the perturbation is achiral, the two plots should be superposable; if the perturbation is chiral, the two plots should not be superposable because the two biphenyl enantiomers form diastereomeric pairs with the chiral probe.

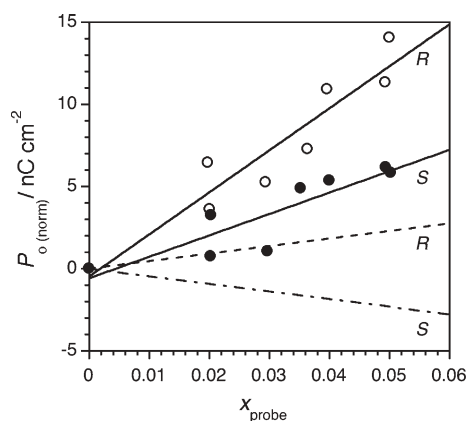
In the three probe experiments featuring **MDW950**, which are shown in Fig. 12, the  $P_o$  vs  $x_{\text{probe}}$  plots in the presence of dopants **7b**, **10** and **8e** are approximately linear up to  $x_{\text{probe}} = 0.25$ , but deviate from linearity beyond that, which may be due to a cooperative effect that partially counters the perturbation of the chiral biphenyl dopant. If one excludes the data points at  $x_{\text{probe}} > 0.25$ , the results of the first two experiments suggest that the 2,2'-dinitro dopants **7b** and **10** exert relatively weak perturbations in the host **PhP1**. The two plots also suggest that the perturbation exerted by the unbridged dopant **7b** is essentially achiral, whereas that exerted by the bridged dopant **10** has some chiral character, which is consistent with the observation that **10** induces a tighter helical pitch in **PhP1** than **7b**. On the other hand, the results of the probe experiment with the 3,3'-dinitro dopant **8e** suggest that it exerts much stronger chiral perturbations in the host **PhP1**. As shown in Fig. 12c,  $\delta_{\text{probe}}$  decreases from  $-435 \text{ nC cm}^{-2}$  to  $-78 \text{ nC cm}^{-2}$  in the presence of (*R*)-**8e**, but increases to  $-605 \text{ nC cm}^{-2}$  in the presence of (*S*)-**8e**.

To determine whether the chiral perturbation has a feedback effect on the polar order of the chiral biphenyl dopant, another probe experiment was carried out using the 3,3'-dimethyl dopant **11**, which is thought to induce much weaker chiral perturbations than **8e** based on helical pitch measurements.<sup>64</sup> In this experiment, the polarization powers of (*R*)-**11** and (*S*)-**11** were measured in the presence of (*S*)-**8e** at a constant mole fraction  $x_d = 0.04$ ; the  $P_o$  values were normalized by subtracting the calculated  $P_o$  contribution from (*S*)-**8e** (Fig. 13). The results show that the perturbation exerted by (*S*)-**8e** influences the polarization powers of (*R*)- and (*S*)-**11** in very different ways: it amplifies  $\delta_{\text{probe}}$  by a factor of 5.5 in the case of (*R*)-**11**, and by a factor of 2.8 in the case of (*S*)-**11**, but also causes an inversion of the sign of polarization induced by the latter! These results demonstrated that a chiral perturbation exerted by one chiral biphenyl dopant can amplify the



**Fig. 12** Reduced polarization  $P_o$  vs mole fraction of **MDW950** in **PhP1** at  $T - T_C = -5$  K in the presence of (a) dopant (+)-**7b** (filled circles) and (–)-**7b** (open circles) at  $x_d = 0.04$ , (b) dopant (+)-**10** (open circles) and (–)-**10** (filled circles) at  $x_d = 0.04$ , and (c) dopant (*R*)-**8e** (filled circles) and (*S*)-**8e** (open circles) at  $x_d = 0.04$ . The dashed lines correspond to the least-squares fit of the reference plot for **MDW950** shifted along the  $y$ -axis by a value equal to  $P_o$  at  $x_{\text{probe}} = 0$ . In plot (c), the solid lines represent the least-squares fits for the data points, excluding those at  $x_{\text{probe}} = 0.30$ .





**Fig. 13** Normalized reduced polarization  $P_{o(\text{norm})}$  vs mole fraction of (*R*)-**11** (○) and (*S*)-**11** (●) in **PhP1** at  $T - T_C = -5$  K in the presence of dopant (*S*)-**8e** at  $x_d = 0.04$ . The  $P_{o(\text{norm})}$  values were obtained by subtracting the calculated  $P_o$  induced by (*S*)-**8e** from the total  $P_o$ . The solid lines correspond to the least-squares fits of the two plots and the dashed lines correspond to the least-squares fit of the reference plots for (*R*)-**11** (---) and (*S*)-**11** (- · -).

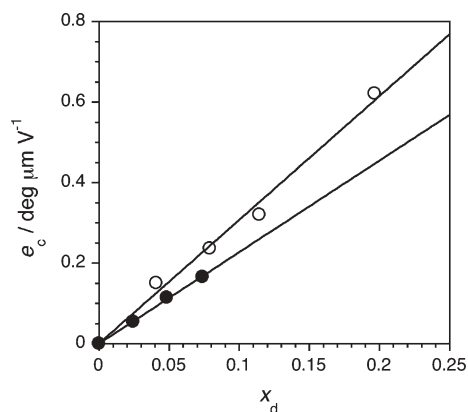
polarization power of another, and thus provided the first experimental evidence of the CTF effect.

### Electroclinic power of axially chiral biphenyl dopants

In general, chiral SmA\* liquid crystals with large electroclinic coefficients  $e_c$  exhibit large spontaneous polarizations in the SmC\* phase. Hence, a logical progression of the research on axially chiral biphenyl dopants was to investigate their 'electroclinic power'  $\delta_e$  (eqn. 7) in the SmA phase of different liquid crystal hosts, and determine whether  $\delta_e$  exhibits the same host dependence as the polarization power  $\delta_p$ .<sup>71</sup>

$$\delta_e = \left( \frac{de_c(x_d)}{dx_d} \right)_{x_d \rightarrow 0} \quad (7)$$

As shown in Fig. 14, the electroclinic coefficients measured as a function of  $x_d$  for mixtures of the chiral dopant (*R*)-**8e** in **PhP1** and **NCB76** gave good least-squares fits corresponding to  $\delta_e$  values of 3.1 and 2.3 deg  $\mu\text{m V}^{-1}$ , respectively, which are

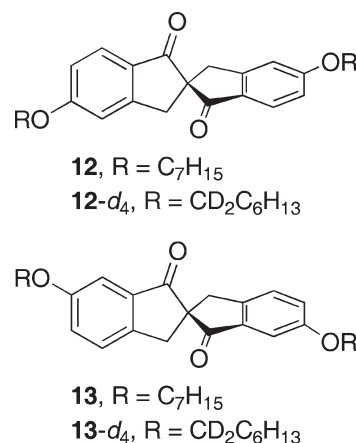


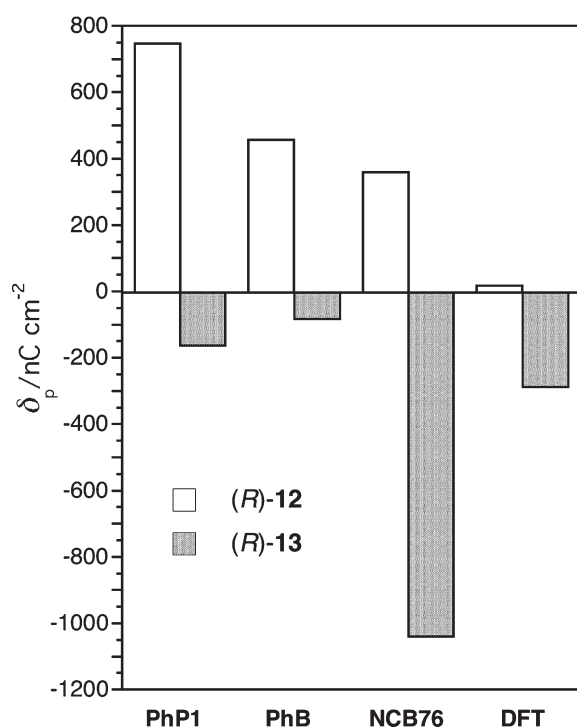
**Fig. 14** Electroclinic coefficient  $e_c$  vs mole fraction of (*R*)-**8e**  $x_d$  in **PhP1** (○) and **NCB76** (●) measured at  $T - T_C = +5$  K.

of the same order of magnitude as the highest electroclinic coefficients for neat SmA\* liquid crystals (on the order of 6–7 deg  $\mu\text{m V}^{-1}$  at the same reduced temperature).<sup>39</sup> However, the difference in  $\delta_e$  values in the two different hosts is much smaller than the corresponding difference in  $\delta_p$  values (–1555 vs –514 nC cm<sup>-2</sup>, respectively), which suggests that the CTF effect does not play as important a role in the SmA\* phase as in the SmC\* phase. To determine the influence of chiral perturbations exerted by (*R*)-**8e** on the induced electroclinic effect, we performed probe experiments using mixtures of (*R*)-**8e** ( $x_d = 0.04$ ) and either the (*R*) or (*S*) enantiomer of the probe dopant **11** in **PhP1** at  $T - T_C = +5$  K. Interestingly, we found no significant difference in  $e_c$  values for the (*R,R*) and (*R,S*) dopant/probe combinations, which suggests that any chiral perturbations exerted by (*R*)-**8e** in the SmA\* phase under an electric field are on a much shorter length scale than in the SmC\* phase, perhaps due to less effective core–core interactions. This is consistent with previous observations that molecules tilt as rigid rods in the SmA\* phase under an electric field, and are therefore more prone to out-of-layer fluctuations than in the SmC\* phase.<sup>72,73</sup>

### Polarization power of axially chiral 2,2'-spirobiindan-1,1'-dione dopants

Despite the high polarization powers achieved with axially chiral biphenyl dopants such as **8d** in the complementary host **PhP1**, there is an inherent flaw in their design: rotation of the polar biphenyl core with respect to the two ester side-chains can be readily achieved when confined to the binding site of the host, without affecting the shape of the dopant (Fig. 9). To address this design flaw, we recently shifted our focus on dopants with an axially chiral 2,2'-spirobiindan-1,1'-dione core such as **12** and **13** which lack a single rotational axis spanning the entire length of the core.<sup>74</sup> As shown in Fig. 15, the polarization powers of these two dopants show pronounced Type II behavior. The polarization power of the 5,5'-diheptyloxy isomer (*R*)-**12** is uniformly positive in the four liquid crystal hosts and ranges from +749 nC cm<sup>-2</sup> in **PhP1** to +21 nC cm<sup>-2</sup> in **DFT** at  $T - T_C = -10$  K. On the other hand, the polarization power of the 6,6'-diheptyloxy isomer (*R*)-**13** is uniformly negative and ranges from –79 nC cm<sup>-2</sup> in **PhB** to –1037 nC cm<sup>-2</sup> in **NCB76** at  $T - T_C = -10$  K.

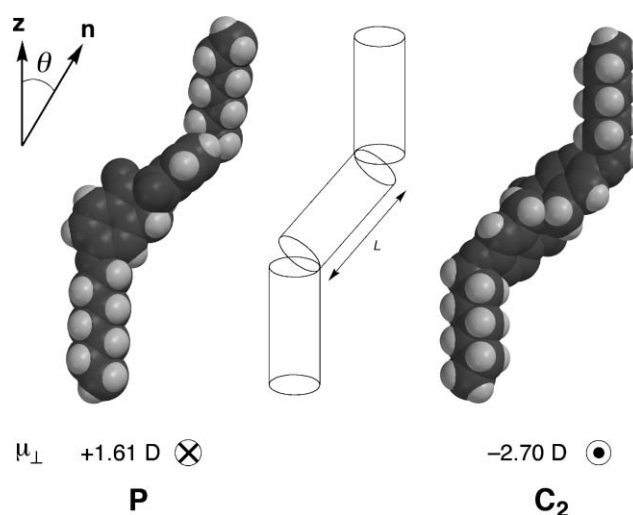




**Fig. 15** Polarization powers  $\delta_p$  of dopants (R)-12 and (R)-13 in the hosts PhP1, PhB, NCB76 and DFT at  $T - T_C = -10$  K.

A detailed conformational analysis based on the Boulder model suggests that, in the SmC\* phase, both dopants **12** and **13** are in equilibrium between two zigzag conformations with opposite transverse dipole moments  $\mu_{\perp}$ , as shown for (R)-12 in Fig. 16. In one conformation (**P**), the plane of one indanone fragment is congruent with the tilt plane defined by **n** and **z** and the  $\mu_{\perp}$  orientation corresponds to a positive  $P_S$ ; in the other conformation (**C<sub>2</sub>**), the  $C_2$  axis of the core is coincident with the polar axis and the  $\mu_{\perp}$  orientation corresponds to a negative  $P_S$ . The only structural difference between **P** and **C<sub>2</sub>** lies in the conformation of one alkoxy side-chain. In the **C<sub>2</sub>** conformer, each alkoxy group is *syn*-periplanar relative to the carbonyl group, and features a *gauche* bend along the C–O bond axis; in the **P** conformer, one alkoxy group is *syn*-periplanar with a *gauche* bend while the other is *anti*-periplanar relative to the carbonyl group, with no *gauche* bend. In the gas phase, the difference in energy between these two conformers is very subtle; heat of formation values calculated for **P** and **C<sub>2</sub>** at the AM1 level are within 0.1 kcal mol<sup>-1</sup>. However, according to the Boulder model, this conformational distribution is likely to be skewed towards the conformation that provides the best fit to the binding site of the liquid crystal host. The conformational analysis for (R)-13 gave essentially the same results as that for (R)-12, except that the corresponding **P** and **C<sub>2</sub>** conformers have opposite  $\mu_{\perp}$  orientations with respect to the polar axis, which is consistent with the difference in sign of polarization induced by the two dopants. A correlation of the sign of  $P_S$  with the absolute configuration of each dopant suggests that the **P** conformer is favored over the **C<sub>2</sub>** conformer in the SmC\* phase.

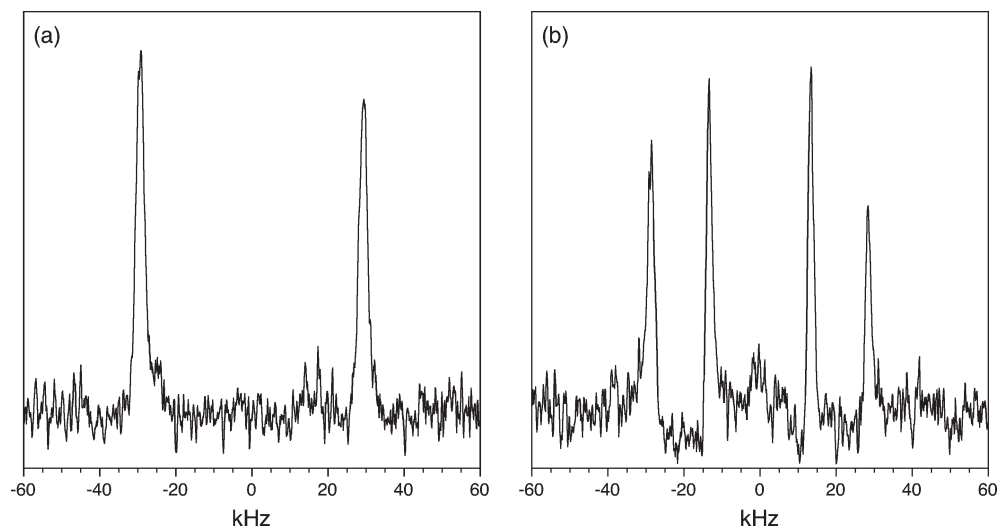
Despite the similarity in conformational distributions predicted by the conformational analyses of the 5,5'- and



**Fig. 16** Space-filling models of the **P** and **C<sub>2</sub>** conformations of (R)-12 in relation to a simplified form of the binding site in three cylindrical sections. The dipole moments along the polar axis ( $\mu_{\perp}$ ) were calculated for each minimized structure at the AM1 level. The polar axis is normal to the plane of the page.

6,6'-dialkoxy isomers, the observed trends in polarization power vs host structures are very different (Fig. 15); especially noteworthy is the high  $\delta_p$  value of  $-1037$  nC cm<sup>-2</sup> obtained for (R)-13 in NCB76. Probe experiments performed with MDW950 in NCB76 suggest that both (R)-12 and (R)-13 exert relatively weak long-range perturbations that are achiral in nature. However, <sup>2</sup>H NMR experiments performed on mixtures of the deuterated racemic dopants (RS)-12-*d*<sub>4</sub> and 13-*d*<sub>4</sub> suggest that the 6,6'-dialkoxy isomer does exert *short-range* chiral perturbations. As shown in Fig. 17, the <sup>2</sup>H NMR spectrum of a 10 mol% mixture of (RS)-12-*d*<sub>4</sub> in NCB76 at  $T - T_C = -10$  K features the expected quadrupolar doublet with a splitting  $\Delta\nu_Q$  of 58 kHz, which is consistent with the orientational order imposed on the dopant by the SmC phase of the host. On the other hand, the <sup>2</sup>H NMR spectrum of a 5 mol% mixture of (RS)-13-*d*<sub>4</sub> features a pair of doublets with a difference in quadrupolar splitting  $\Delta\Delta\nu_Q$  of 32 kHz. A similar effect was observed by Samulski and others for enantiotopic CD<sub>2</sub> groups in achiral molecules dissolved in a chiral nematic liquid crystal formed by a solution of poly- $\gamma$ -benzyl-L-glutamate (PBLG) in CH<sub>2</sub>Cl<sub>2</sub>, which was attributed to a difference in orientational order parameter of the two C–D bonds due to a reduction in symmetry of the anisotropic solute–solvent interaction potential.<sup>75,76</sup> In the case of (RS)-13-*d*<sub>4</sub>, the pair of quadrupolar doublet may be attributed to a chiral perturbation exerted by the dopant on the liquid crystal host that creates the local chiral environment required to make the pro-*R* and pro-*S* deuterons nonequivalent. Warming the mixture from the SmC\* to the N\* phase resulted in a 60% decrease in  $\Delta\Delta\nu_Q$ , which is consistent with a loss of translational order in the nematic phase that should make chirality transfer *via* core–core interactions less effective.

If one assumes that chirality transfer does not contribute to the polarization induced by (R)-12, the dependence of  $\delta_p$  on the nature of the host may be understood in terms of a shift in the conformational equilibrium between **P** and **C<sub>2</sub>** that



**Fig. 17**  $^2\text{H}$  NMR spectra (92 MHz) of a (a) 10 mol% mixture of  $(RS)\text{-}12\text{-}d_4$  in **NCB76** and (b) 5 mol% mixture of  $(RS)\text{-}13\text{-}d_4$  in **NCB76** at  $T - T_C = -10$  K.

depends on the dimension of the core section of the binding site  $L$  (Fig. 16). The corresponding core section length of each conformer may be approximated by the distance between atomic coordinates where divergence from the central cylindrical space begins; this approximation reveals that the core section of the **P** conformer is *ca* 1.5 Å shorter than that of the **C<sub>2</sub>** conformer. According to this model, the conformational equilibrium should shift toward the **P** conformer (positive  $\mu_{\perp}$ ) as  $L$  becomes shorter, which is consistent with the trend in  $\delta_p$  observed for  $(R)\text{-}12$ : it ranges from +21 nC cm<sup>-2</sup> in the host with the longest core (**DFT**,  $L = 14.4$  Å) to +749 nC cm<sup>-2</sup> in the host with the shortest core (**PhP1**,  $L = 9.7$  Å). Thus, the 5,5'-dialkoxy isomer appears to behave primarily as a *passive* dopant with a conformational distribution that adapts to changes in the dimension of the binding site, which represents a new form of supramolecular recognition in an anisotropic fluid. On the other hand, the different trend in  $\delta_p$  observed for the 6,6'-dialkoxy isomer may be ascribed to the added contribution of local chiral perturbations according to the CTF model. What is remarkable in the case of the spirobiindan-1,1'-dione dopants is how a relatively minor change in dopant structure such as moving the alkoxy side-chains from the 5,5' to the 6,6' positions can affect not only the magnitude but also the sign of  $\delta_p$ , without changing the absolute configuration of the stereo-polar unit.

## Summary

The spontaneous polarization induced by dopants with axially chiral cores shows a pronounced dependence on the core structure of the liquid crystal host. Such a manifestation of molecular recognition reflects the nanosegregation of aromatic cores from paraffinic side-chains in the SmC phase, and the collective effect of relatively weak intermolecular interactions in ordered fluids. In the case of dopants with axially chiral biphenyl cores, this host dependence can be rationalized based on the propensity of the dopant to exert perturbations on the liquid crystal host that may be chiral in nature, depending on

the complementarity of dopant and host core structures to undergo chirality transfer. Probe experiments have shown that a dopant with an axially chiral biphenyl core can exert strong chiral perturbations in a liquid crystal host with a complementary phenylpyrimidine core, and that such perturbations can enhance the induced polarization as a 'Chirality Transfer Feedback' effect. Interestingly, the CTF effect does not appear to influence the electroclinic response of the same mixtures in the SmA\* phase, which suggests that chiral perturbations are on a much shorter length scale than in the SmC\* phase.

We have shown that a relatively minor change in the structure of dopants with axially chiral 2,2'-spirobiindan-1,1'-dione cores, *i.e.*, moving the alkoxy side-chains from the 5,5' to the 6,6' positions of the core, has profound effects on the sign and magnitude of the induced polarization, and on the propensity of the dopant to exert chiral perturbations on the liquid crystal host. An analysis of conformations that 'fit' the binding site of the Boulder model suggests that the polarization power depends on an equilibrium between two conformations of opposite polarity relative to the polar axis, and that the observed host dependence may be understood in terms of differences in steric demand between the two conformations in the core section of the binding site. We have also demonstrated the usefulness of  $^2\text{H}$  NMR spectroscopy to probe the local environment of dopant molecules and detect short-range chiral perturbations exerted by a dopant on the liquid crystal host. These studies suggest that rational design of chiral dopants with very high polarization powers may be achieved by careful mixing and matching of dopant and host core structures based on principles of molecular recognition.

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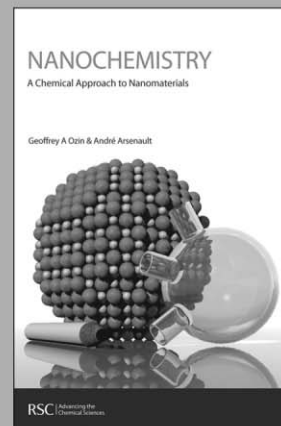
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