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Large electroclinic effect in SmA* liquid crystals induced by an atropisomeric biphenyl dopant

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Electroclinic coefficients (e_c) and reduced polarizations (P_o) were measured in the SmA* and SmC* liquid crystal phases formed by 4 mol% mixtures of the chiral dopant (–)-2,2′,6,6′-tetramethyl-3,3′-dinitro-4,4′-bis[(4-nonyloxybenzoyl)oxy]biphenyl [(–)-1] in the binary host mixture of 5-(4-butyloxyphenyl)-2-octyloxypyrimidine (5-PhP1) and 2-(4-butyloxyphenyl)-5-octyloxypyrimidine (2-PhP1) over the mole fraction range $0 \leqslant x_{\text{5-PhP1}} \leqslant 0.24$. Both e_c and P_o increase with $x_{\text{5-PhP1}}$, which is consistent with the assumption that 5-PhP1 should be more effective in propagating chiral perturbations exerted by (–)-1. At $x_{\text{5-PhP1}} = 0.24$ and $T - T_C = +5$ K, the electroclinic coefficient is 0.34° μm V^{-1}, which is one order of magnitude greater than the highest e_c value previously reported for a chiral dopant at the same mole fraction and reduced temperature.

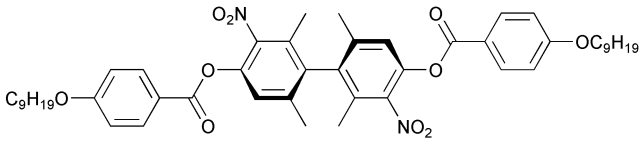
The smectic A liquid crystal phase is characterized by a layer structure in which rod-like mesogens are oriented with their long axes perpendicular to the layer plane. In the absence of an electric field, a smectic A phase formed by chiral mesogens (SmA*) cannot be distinguished from an achiral SmA phase using conventional characterization methods such as polarized microscopy. However, one can make this distinction based on the electroclinic effect, which occurs only in the chiral SmA* phase. In the electroclinic effect, an electric field applied parallel to the layer plane induces a tilt of the molecular long axes with respect to the layer normal in a direction orthogonal to the field.[1] The electroclinic effect is described by a phenomenological model derived from Landau theory which predicts a linear dependence of the induced tilt angle (θ) on the applied field (E) at low field strengths.[2,3] This relationship is expressed by eqn. 1 and 2,

$$\theta = e_c E \tag{1}$$

$$e_c = \frac{c}{\alpha(T - T_C)} \tag{2}$$

where e_c is the electroclinic coefficient, c is the electroclinic coupling constant between θ and E, and $\alpha(T - T_C)$ is the first coefficient of the Landau free-energy expansion. The term α is a susceptibility coefficient controlling the molecular tilt, which is independent of chirality,[4] and T_C is the temperature corresponding to the second-order transition from the orthogonal SmA* to the tilted SmC* phase. The relationship between θ and E normally deviates from linearity at high field strengths and/or when the system approaches T_C.

Because the electroclinic response scales linearly with E at low field strengths and shows no bistability, it is possible to generate a continuous grey-scale controlled by an applied voltage. In addition, electroclinic switching is typically 100 times faster than Goldstone-mode switching in ferroelectric SmC* liquid crystals, which makes SmA* materials suitable for a wide range of electro-optical device applications, including micro-color filters, tunable color filters, and spatial light modulators.[5] In order to develop electroclinic SmA* materials for device applications, many groups have focused their efforts on the design of SmA* mesogens with high electroclinic coefficients,[6–9] including so-called de Vries SmA* materials, which undergo electroclinic switching without layer shrinkage.[10–12] However, the design of chiral SmA* materials suitable for device applications requires not only the optimization of chiral bulk properties such as e_c, but also of achiral bulk properties such as the mesophase temperature range. A solution to this problem, which is widely used in the formulation of ferroelectric SmC* materials for display applications, is to combine a chiral dopant capable of inducing the desired electroclinic response at low concentration with an achiral SmA liquid crystal host mixture. Surprisingly, only two reports of electroclinic induction by chiral dopants have been published thus far.[13,14] In this Communication, we report the induction of a relatively large electroclinic effect in SmA* liquid crystal mixtures using a chiral dopant with an atropisomeric biphenyl core.



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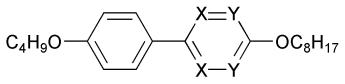

2-PhP1, X=N, Y=CH; Cr 58 SmC 85 SmA 95 N 98 I
5-PhP1, X=CH, Y=N; Cr 84 SmA 117 I

In general, SmA* materials with large electroclinic responses also exhibit large spontaneous polarizations in the SmC* phase.[7–9] We have shown that atropisomeric biphenyl dopants such as (–)-**1** induce remarkably high spontaneous polarizations in the 2-phenylpyrimidine host 2-PhP1 due to a high propensity of the atropisomeric biphenyl cores to exert a chiral perturbation on surrounding host molecules *via* core–core conformational interactions.[15] In 2-PhP1, the chiral perturbation is thought to propagate *via* a distortion of the 2-phenylpyrimidine core from a planar conformation in the ground state to a twisted homochiral conformation. Recent probe experiments suggest that such chiral perturbations amplify the spontaneous polarization by causing a shift in the conformational equilibrium of the chiral dopant, favoring one orientation of the transverse dipole moment along the polar axis.[16] To further test this model and assess its relevance on the

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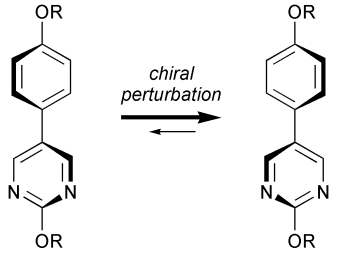

Fig. 1 Proposed effect of a chiral perturbation on the core structure of 5-PhP1.

electroclinic effect in the SmA* phase, we carried out measurements of the reduced polarization (P_o)[17] and electroclinic coefficient (e_c) in the SmC* and SmA* phases formed by 4 mol% mixtures of (–)-**1** in the binary host mixture formed by 2-PhP1 and the corresponding 5-phenylpyrimidine 5-PhP1 over the mole fraction range $0 \leqslant x_{5\text{-PhP1}} \leqslant 0.24$. These experiments are based on the assumption that chiral perturbations exerted by the dopant (–)-**1** should propagate more effectively in 5-PhP1 by causing a shift in the conformational equilibrium of the twisted 5-phenylpyrimidine core towards one enantiomeric conformation instead of causing a chiral distortion of the planar 2-phenylpyrimidine core (Fig. 1).[18]

Observations by polarized microscopy revealed that an increasing proportion of 5-PhP1 in the host mixture causes the nematic phase and then the SmC phase of 2-PhP1 to vanish at $x_{5\text{-PhP1}} > 0.1$ and 0.3, respectively. In order to normalize the e_c values with respect to T_C, the presence of an underlying SmC* phase was required and electroclinic measurements were therefore limited to $x_{5\text{-PhP1}} \leqslant 0.24$. Good alignment in polyimide-rubbed ITO glass cells with a 4 μm spacing (Displaytech, Inc.) was achieved for all doped liquid crystal mixtures by slow cooling from the isotropic liquid phase while applying a 3 Hz triangular wave ac field. The electroclinic tilt θ was measured as a function of E by polarized microscopy at $T - T_C = +5$ K while applying a 0.1 Hz square wave ac field. Values of θ were taken as half the rotation angle between two extinction positions corresponding to opposite signs of E. The resulting θ *vs.* E plots gave good least-squares fits ($R^2 = 0.980$–0.998) from which e_c values were derived (Fig. 2). The reduced polarization P_o was measured as a function of $x_{5\text{-PhP1}}$ at $T - T_C = -5$ K by the polarization reversal current method, which is described in detail elsewhere.[19]

As shown in Fig. 3, both the electroclinic coefficient e_c and absolute value of P_o increase with $x_{5\text{-PhP1}}$, which is consistent

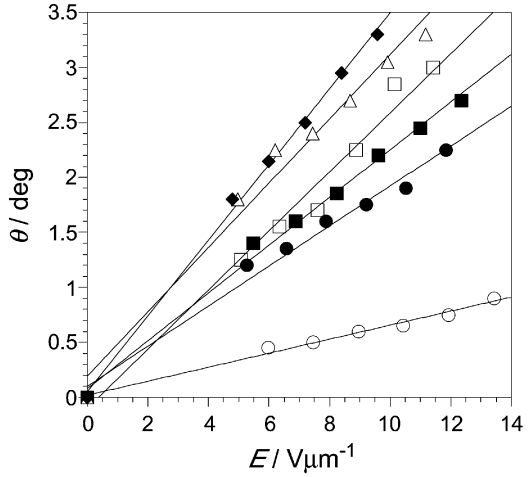

Fig. 2 Electroclinic tilt angle (θ) *vs.* applied electric field (E) for 4 mol% mixtures of (–)-**1** in the binary host mixture 5-PhP1–2-PhP1 at $T - T_C = +5$ K. $x_{5\text{-PhP1}} = 0.0$ (O), 0.05 (●), 0.094 (□), 0.14 (■), 0.19 (Δ), 0.24 (◆).

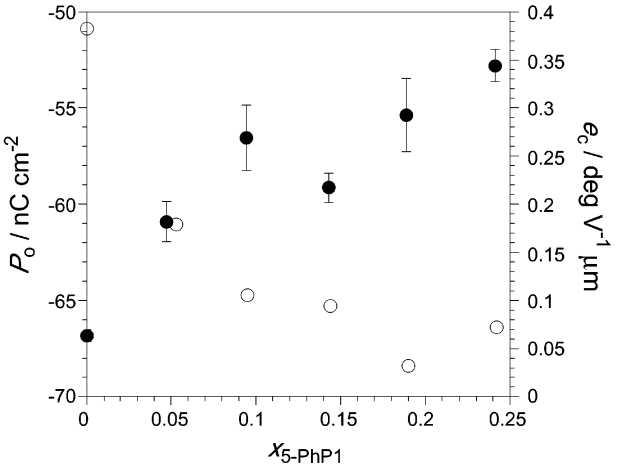

Fig. 3 Reduced polarization [P_o (O)] and electroclinic coefficient [e_c (●)] *vs.* mole fraction of 5-PhP1 ($x_{5\text{-PhP1}}$) at $T - T_C = -5$ and +5 K, respectively. Error bars represent ±2 standard errors.

with the assumption that chiral perturbations should propagate more effectively in 5-PhP1. It is also possible that the increase in e_c is due in part to a change in tilt susceptibility (α) that is unrelated to chiral perturbations.[4] More importantly, a comparison of the e_c values with those found in the literature suggests that the propensity of dopant (–)-**1** to induce an electroclinic effect in 5-PhP1–2-PhP1 mixtures is the highest reported heretofore. At $x_{5\text{-PhP1}} = 0.24$, the electroclinic coefficient is 0.34° μm V^{-1}, which is one order of magnitude greater than the highest value previously reported for a chiral dopant at the same mole fraction and reduced temperature.[14] Unfortunately, given the paucity of such studies, it is difficult to appreciate the magnitude of the electroclinic effect induced by (–)-**1**. Extrapolation of e_c to a dopant mole fraction of 1.0 gives a value of 8.5° μm V^{-1}, which compares favorably with the highest electroclinic coefficient obtained for neat SmA* liquid crystals, which is on the order of 6.0° μm V^{-1} at the same reduced temperature.[12] It is likely that the high propensity of (–)-**1** to induce an electroclinic effect in 5-PhP1–2-PhP1 is related to its unique ability to exert a strong chiral perturbation in smectic hosts with a complementary core structure. A more systematic structure–property study of atropisomeric dopants in SmA* liquid crystals and their potential in electroclinic SmA* formulations is in progress and will be reported in due course.

Acknowledgements

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