Enhanced polar ordering in ferroelectric liquid crystals induced by atropisomeric dopants

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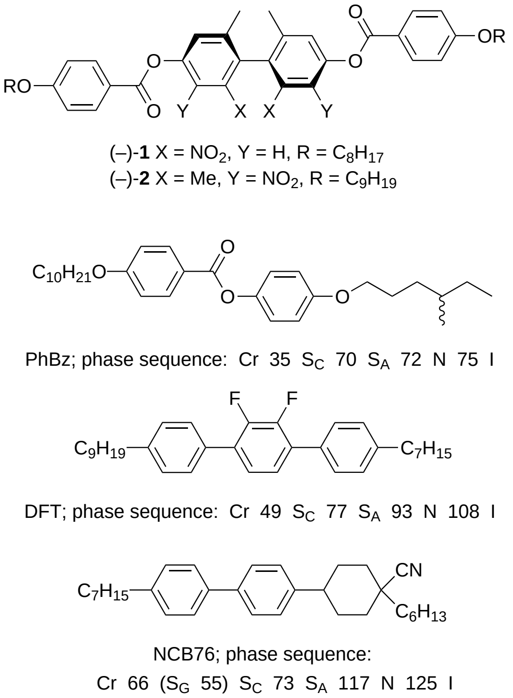
The spontaneous polarization of a S_C* liquid crystal phase induced by atropisomeric dopants with large transverse molecular dipoles exhibits a very strong dependence on the nature of the S_C liquid crystal host.

A ferroelectric smectic C* liquid crystal phase possesses a permanent dipole moment, the spontaneous polarization (P_S), which is a macroscopic manifestation of molecular chirality.[1] The dependence of P_S on the molecular structure of the chiral component(s) of a S_C* phase has received considerable attention over the past 15 years as it relates directly to the performance optimization of FLC light valves and displays.[2–4] In general, ferroelectric liquid crystals suitable for display applications are induced S_C* phases obtained by mixing a chiral dopant with high polarization power (δ_P) in a S_C liquid crystal host mixture with low viscosity and broad temperature range. The polarization power is a measure of the propensity of a chiral dopant to induce a spontaneous polarization in a S_C host as expressed by eqn. (1), in which P_o is the reduced polarization of the FLC and x_d is the dopant mole fraction.[5]† In most cases, the polarization power of a chiral dopant is independent of the nature of the S_C host. However, Stegemeyer has reported several examples of chiral dopants with rigid chiral cores that exhibit a dependence of δ_P on the nature of the S_C host; these compounds are referred to as Type II dopants.[6]

$$\delta_P = \left(\frac{dP_o\,(x_d)}{dx_d}\right)_{x_d \to 0} \qquad (1)$$

Recently, we reported the induction of a S_C* phase by the atropisomeric dopant (−)-**1**, which exhibited a pronounced Type II host dependence in the S_C liquid crystal hosts PhBz and NCB76 (Fig. 1).[7] We proposed that polar ordering of (−)-**1** in the S_C lattice originates from a small asymmetric bias in the rotation of the biphenyl core about the ester C–O bonds, which we estimated by AM1 calculations on the model compound 3-methyl-5-nitrophenyl benzoate at 0.4 kcal mol^{-1} (1 cal = 4.184 J). We have extended this conformational analysis to other phenyl benzoate derivatives as model compounds, and found that shifting the symmetry-breaking NO_2 group to the *ortho*-position with respect to the ester group raises the rotational bias about the ester C–O bond to 1.1 kcal mol^{-1}. In order to test the validity of this conformational analysis in predicting the relative polar ordering of atropisomeric dopants, and to further investigate the generality of Type II behaviour in these systems, we have synthesized the dopant (−)-**2** in optically pure form and measured its polarization power in the S_C hosts PhBz,[8] NCB76 (E. Merck) and DFT.[9]

The precursor **5** was synthesized in racemic form starting with the known benzidine **3**,[10] as shown in Scheme 1, and resolved by chiral stationary phase HPLC using a Daicel Chiralcel OJ column to give the (−) enantiomer in optically pure form.‡ The latter was esterified under mild conditions using DCC/DMAP to give the diester (−)-**2**, which showed no liquid crystalline behaviour by differential scanning calorimetry. Compound (−)-**2** was doped in the S_C hosts PhBz, DFT and NCB76 at four different concentrations in the range $0.01 < x_d < 0.05$. Each mixture was introduced into polyimide-coated ITO glass cells with a 4 μm gap, and aligned by slow cooling from isotropic liquid to the S_C* phase at $T–T_{AC} = -5$ °C. Spontaneous polarization and tilt angle (θ) values were measured as a function of x_d by the triangular wave method using a Displaytech APT II polarization testbed (100 Hz, 6 V μm^{-1}).[11] At $x_d = 0.03$, the dopant (−)-**2** gave a P_S value of −2.5 nC cm^{-2} (θ = 9.5°) in NCB76, and a P_S value of −1.7 nC cm^{-2} (θ = 10.5°) in DFT. In these two hosts, a plot of P_o *vs.* x_d gave a good linear fit, from which δ_P values were



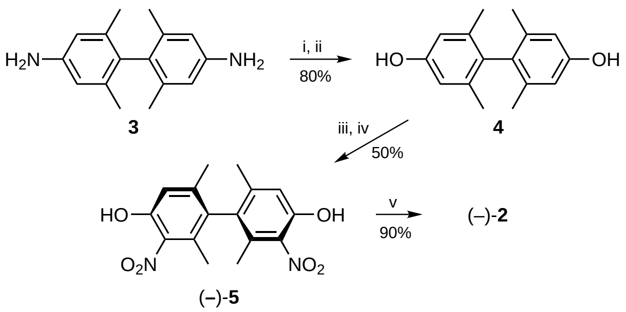
(−)-**1** X = NO_2, Y = H, R = C_8H_{17}
(−)-**2** X = Me, Y = NO_2, R = C_9H_{19}

PhBz; phase sequence: Cr 35 S_C 70 S_A 72 N 75 I

DFT; phase sequence: Cr 49 S_C 77 S_A 93 N 108 I

NCB76; phase sequence:
Cr 66 (S_G 55) S_C 73 S_A 117 N 125 I

Fig. 1



Scheme 1 *Reagents and conditions*: i, $NaNO_2$, HCl, 5 °C; ii, 10% H_2SO_4, reflux; iii, $Fe(NO_3)_3 \cdot 9H_2O$, EtOH, reflux; iv, chiral stationary phase HPLC resolution, semiprep Daicel Chiralcel OJ column, hexanes–EtOH 9 : 1, 3 ml min^{-1}; v, 4-nonyloxybenzoic acid, DCC, DMAP, CH_2Cl_2, 25 °C

obtained (Fig. 2).† In the host PhBz, P_S was too low to be measured at $x_d = 0.05$; an upper limit value for δ_P was estimated based on the instrument detection limit (0.3 nC cm^{-2}) and an observed tilt angle of 10° at $T–T_{AC} = -5$ °C. These results are presented in Table 1, including previously unreported data for dopant (−)-**1** in DFT, and correlated with dielectric anisotropy values ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) measured in the nematic phase for structurally analogous mesogens.§ The $\Delta\varepsilon$ values are consistent with the increase in transverse dipole moment of the mesogens in the order PhBz < DFT < NCB76.

In NCB76 and DFT, the dopant (−)-**2** shows a much higher polarization power than (−)-**1**, which is consistent with the increase in rotational bias about the ester C–O bond predicted by the AM1 calculations. Furthermore, (−)-**2** exhibits a very strong dependence of δ_P on the nature of the S_C host. To the best of our knowledge, the > 15-fold enhancement in polarization power shown by (−)-**2** as a function of the S_C host is the largest thus far reported for a Type II dopant. For each dopant, a correlation exists between the polarization power and the dielectric anisotropy of the S_C host, which suggests that the Type II dependence observed in this case arises from enhanced coupling of the dopant with the S_C lattice *via* transverse dipole–dipole interactions. This coupling mechanism is likely to induce polar ordering of the S_C host and cause an asymmetric distortion of the achiral S_C lattice that further enhances rotational ordering of the atropisomeric core. We plan to continue testing the validity of this model through the design and characterization of new series of atropisomeric dopants analogous to **1** and **2**.

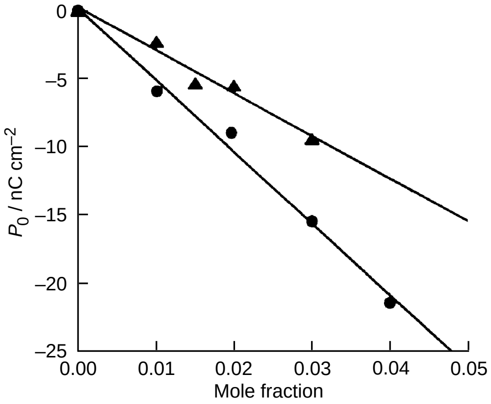


Fig. 2 Reduced polarization P_o as a function of mole fraction for the dopant (−)-**2** in the S_C hosts NCB76 (circles) and DFT (triangles) at $T–T_{AC} = -5$ °C

Table 1 Polarization power values for dopants (−)-**1** and (−)-**2** in the S_C hosts NCB76, DFT and PhBz

		δ_P/nC cm$^{-2\,a}$			
Host	$\Delta\varepsilon^{b}$	(−)-**1**	sign	(−)-**2**	sign
NCB76	−4.7	170^{c}	+	523	−
DFT	−1.7	63^{d}	+	312	−
PhBz	−0.35	< 20	−	< 34	−

^{a} Measured at $T–T_{AC} = -5$ °C. ^{b} Dielectric anisotropy values measured in the nematic phase for the structural analogues 4-(4′-pentylbiphenyl-4-yl)-1-propylcyclohexanecarbonitrile, 2′,3′-difluoro-4,4″-dipropyl-*p*-terphenyl,[12] and 4-hexyloxyphenyl 4-decyloxybenzoate.[13] ^{c} From ref. 7. ^{d} This value was extrapolated from a single P_o measurement at $x_d = 0.04$.

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Footnotes

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† The reduced polarization is intrinsic to the chiral component(s) of the S_C* phase at a fixed temperature difference below the S_C*–S_A* phase transition ($T–T_{AC}$), and is related to the spontaneous polarization (P_S) and tilt angle (θ) of the S_C* phase by the equation:

$$P_o = P_S/\sin\theta$$

‡ All new compounds gave satisfactory spectral data (^{1}H, ^{13}C NMR and mass spectra) and combustion analyses.

§ Dielectric anisotropy values for PhBz, DFT, NCB76 are currently unavailable.

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