Induction of a Ferroelectric S_C* Liquid Crystal Phase by an Atropisomeric Dopant Derived from 4,4′-Dihydroxy-2,2′-dimethyl-6,6′-dinitrobiphenyl

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Abstract: We report the induction of a ferroelectric S_C* phase in two S_C liquid crystal hosts using a novel chiral dopant (−)-**1** that incorporates an atropisomeric core derived from 4,4′-dihydroxy-2,2′-dimethyl-6,6′-dinitrobiphenyl. The racemic dopant was synthesized in 11 steps with an overall yield of 9% and resolved by chiral stationary phase HPLC in optically pure form. The magnitude and sign of the spontaneous polarization (P_S) induced by (−)-**1** were found to depend strongly on the nature of the S_C host. In a cyclohexanecarbonitrile host, (−)-**1** induces a positive polarization that is measurable over the dopant mole fraction range $0.02 < x_d < 0.044$; in a phenyl benzoate host, (−)-**1** induces a negative polarization that falls below detection limit at $x_d \leq 0.05$. The polarization power (δ_p) of (−)-**1** in the cyclohexanecarbonitrile host is +170 nC/cm^2, which is more than eight times that estimated as upper limit in the phenyl benzoate host. These results are rationalized on the basis of the Boulder model for the molecular origins of P_S by modeling the conformational behavior of the biphenyl core in the achiral lattice of the S_C host using semiempirical AM1 calculations. The dependence of δ_p on the nature of the S_C host is correlated to the large difference in negative dielectric anisotropy ($\epsilon\| - \epsilon\perp$) of the two hosts.

Introduction

The phenomenon of spontaneous polar ordering (ferroelectricity) in chiral smectic C (S_C*) liquid crystals has received considerable attention over the past 15 years due to the vast potential of these materials as active component of fast switching electro-optical light valves and displays.[1] In 1980, Clark and Lagerwall showed that the helix of a S_C* liquid crystal phase spontaneously unwinds between polyimide-coated glass slides to give a surface-stabilized ferroelectric liquid crystal (SSFLC).[2] As predicted theoretically by Meyer and co-workers,[3] the SSFLC exhibits a finite spontaneous polarization (P_S) along a polar axis perpendicular to the tilt plane, which is defined by the orientation of the molecular long axis **n** (director) and the layer normal **z** (Figure 1). This spontaneous polarization is a macroscopic manifestation of molecular chirality and is a function of the molecular structure of the chiral component(s) of the S_C* phase.[4]

Ferroelectric liquid crystals suitable for SSFLC light valve and display applications are usually *induced* S_C* phases, which are obtained by dissolving a chiral dopant with a large transverse molecular dipole into an achiral S_C liquid crystal host mixture with low orientational viscosity and broad temperature range.[5,6]

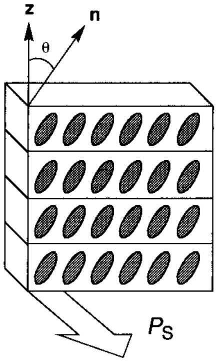

Figure 1. Schematic representation of the SSFLC. The polar axis is ⊥ to the plane of the page.

The spontaneous polarization and tilt angle (θ) of a S_C* phase are related by eq 1 to the reduced polarization (P_o), which is intrinsic to the chiral component of the S_C* phase at a fixed temperature difference below the S_C*-S_A* phase transition (T-T_{AC}).[6] The reduced polarization of an induced S_C* phase generally shows a linear dependence on the mole fraction (x_d) of the chiral dopant at a fixed T-T_{AC}. This relationship is expressed by eq 2, in which the polarization power (δ_p) is a measure of the propensity of a chiral dopant to induce a spontaneous polarization in a S_C host. The polarization power of most chiral dopants is independent of the nature of the achiral S_C host;[6,7] these so-called Type I dopants are usually characterized by an acyclic stereopolar unit located in the side-chain of the molecule. The stereopolar unit consists of the chiral center(s) and all sterically coupled polar functional groups contributing to a transverse molecular dipole. Recently, there have been several reports of S_C* chiral dopants with stereopolar units

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consisting of a chiral ring system located within the rigid core of the molecule.[8] In some of those cases, δ_p has been shown to depend strongly on the nature of the achiral S_C host; these compounds are referred to as Type II dopants.[8a]

$$P_S = P_o \sin\theta \tag{1}$$

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

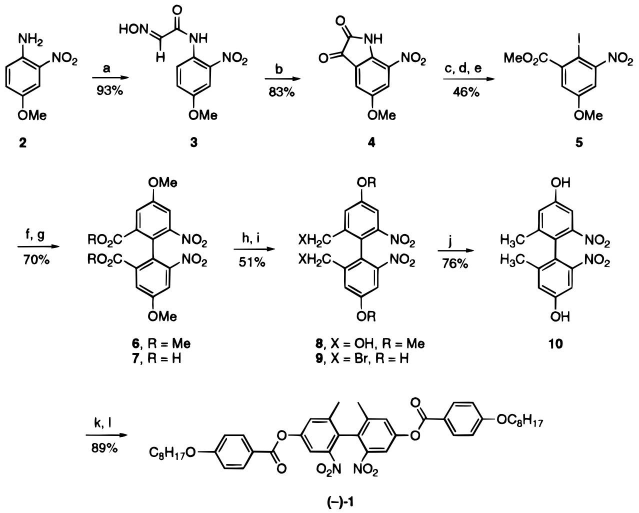
Most of the S_C* mesogens and chiral dopants reported thus far, including Type II dopants, incorporate one or more chiral center(s) in the stereopolar unit. Only a few examples of inherently chiral S_C* mesogens have been reported, which include allene and alkylidenecyclohexane derivatives[9,10] and 1,3-disubstituted ferrocene derivatives.[11] Such compounds are of particular interest due to their potential as high δ_p dopants. In this paper, we introduce a new class of inherently chiral dopant incorporating an atropisomeric biphenyl core with a large transverse dipole moment as the stereopolar unit and report on the dependence of the spontaneous polarization induced by one such compound, (−)-**1**, on the nature of the S_C host.[12]

Results and Discussion

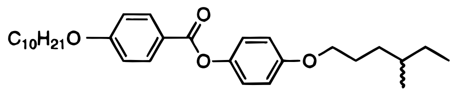
Compound **1** was prepared as a racemic mixture in an overall yield of 9% as shown in Scheme 1. Conversion of **2** to **5** was achieved via modification of a known procedure,[13] followed by an Ullmann coupling and hydrolysis to give the diphenic acid **7**. Selective reduction using BH_3•THF gave the diol **8**, which was converted to the dibromide **9** in a single step and reduced under mild conditions to give the dihydroxybiphenyl **10**. Following esterification, (±)-**1** was resolved by semiprep chiral stationary phase HPLC using a Regis (*S*,*S*)-Whelk-O 1 column to give (−)-**1** in optically pure form.

Thermal analysis by differential scanning calorimetry indicated that (−)-**1** does not exhibit a liquid crystal phase. The dopant (−)-**1** was mixed in the liquid crystal hosts **PhBz** and **NCB76** over the mole fraction range $0.01 < x_d < 0.05$ (Figure 2). The temperature range of the induced S_C* phase in both liquid crystal hosts was found to decrease significantly with increasing dopant mole fraction, with the S_C* phase vanishing completely at $x_d > 0.05$. The doped liquid crystal mixtures were introduced into polyimide-coated ITO glass cells and subjected to a square-wave AC voltage (6 V/μm, 1 Hz) while in the S_C* phase. In each case, the characteristic Goldstone-mode switching of a ferroelectric S_C* phase was observed.[1b,c] No ferroelectric switching was observed in the absence of dopant, nor when (±)-**1** was substituted for (−)-**1**.

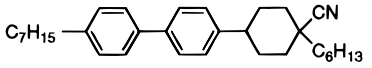
Scheme 1[a]



[a] (a) $Cl_3CCH(OH)_2$, NH_2OH•HCl, Na_2SO_4, H_2O, 55 °C; (b) concentrated H_2SO_4, 95 °C; (c) 30% H_2O_2, NaOH, H_2O, 25 °C; AcOH; (d) $NaNO_2$, concentrated H_2SO_4, 0 °C; KI, H_2O; (e) MeOH, H_2SO_4, reflux; (f) Cu, DMF, reflux; (g) KOH, EtOH, H_2O, reflux; (h) 1.0 M BH_3•THF, 25 °C; (i) 48% HBr, AcOH, reflux; (j) $NaBH_3CN$, HMPA, 55 °C; (k) 4-*n*-octyloxybenzoic acid, DCC, DMAP, CH_2Cl_2, 25 °C; (l) chiral stationary phase HPLC resolution, (*S*,*S*)-Whelk-O 1 column, 40:3:1 hexanes/IPA/CH_2Cl_2, 3 mL/min.



PhBz; phase sequence: X 35 S_C 70.5 S_A 72 N 75 I



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

Figure 2. Structures of S_C hosts and phase transition temperatures in °C.

In the S_C host **PhBz**, the dopant (−)-**1** induced a *negative* spontaneous polarization that fell below the detection limit of our instrumentation (0.2 nC/cm^2) at $x_d \leq 0.05$. Extrapolation of the 0.2 nC/cm^2 detection limit from $x_d = 0.05$ to $x_d = 1$ (factoring in the observed tilt angle) gives an estimated upper limit for $|\delta_p|$ of 20 nC/cm^2 in the S_C host **PhBz**. In the S_C host **NCB76**, the dopant (−)-**1** induced a *positive* spontaneous polarization that was measurable over the mole fraction range $0.02 < x_d < 0.044$. Spontaneous polarization and tilt angle values were measured as a function of temperature at three different concentrations (Figure 3). Reduced polarization values were calculated from P_S and θ values at $T-T_{AC} = -5$ °C using eq 1. A plot of P_o vs x_d shows a positive deviation from linearity (Figure 4), with a δ_p value of +170 nC/cm^2. A similar deviation from linearity for the function P_o (x_d) has been observed previously for Type I and II mesogenic chiral dopants with strong transverse dipole moments, albeit over a much wider mole fraction range, and rationalized on the basis of a local field effect.[7,8a]

The results can be rationalized by considering the Boulder model for the molecular origins of spontaneous polar ordering in S_C* phases.[4] According to this model, (−)-**1** should fit in the achiral lattice (binding site) of a S_C host in a transoid conformation, in which the atropisomeric biphenyl core should be relatively free to rotate with respect to the ester side-chains, giving rise to diastereomeric rotational states (Figure 5). In this lowest energy conformation, (−)-**1** should induce a spontaneous

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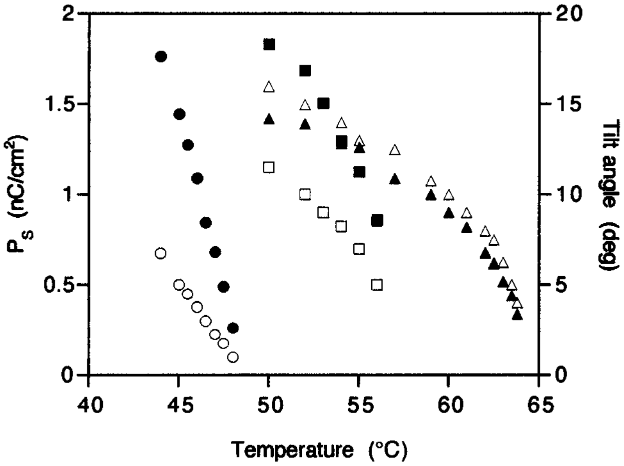

Figure 3. Spontaneous polarization P_S (filled symbols) and tilt angle (open symbols) as a function of temperature for the induced S_C* phase of (−)-**1**/**NCB76** mixtures: $x_d = 0.02$ (triangles), 0.031 (squares), 0.044 (circles).

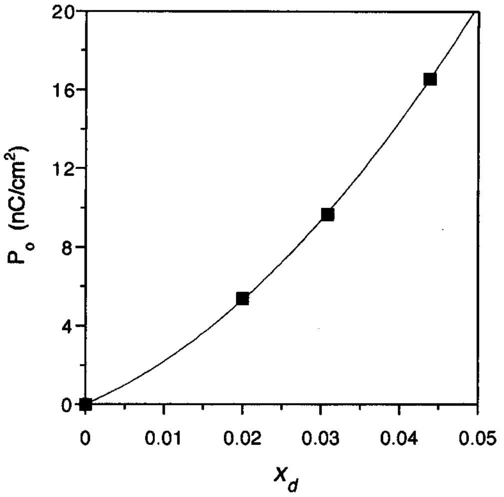

Figure 4. Reduced polarization P_o as a function of dopant mole fraction x_d for the induced S_C* phase of (−)-**1**/**NCB76** mixtures at $T\text{-}T_{AC} = -5$ °C.

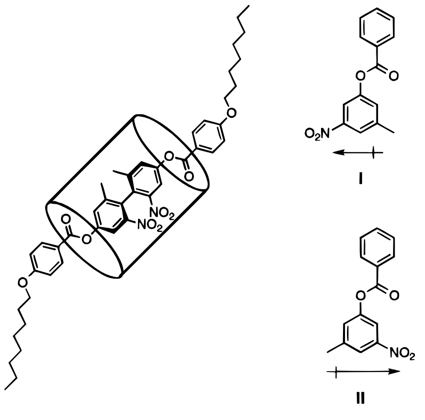

Figure 5. Transoid conformation of (−)-**1** in the achiral lattice of a S_C host according to the Boulder model (left); the polar axis is ⊥ to the plane of the page. Structures representing the time-average conformational minima of 3-methyl-5-nitrophenyl benzoate for rotation about the ester C−O bond according to AM1 calculations (right).

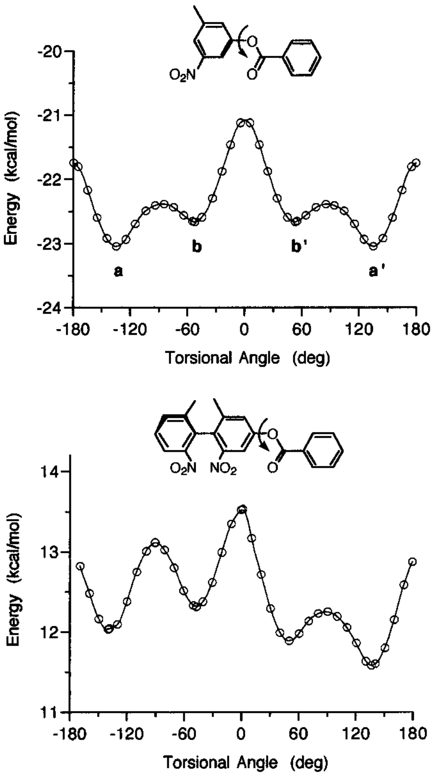

Figure 6. Energy profiles for 3-methyl-5-nitrophenyl benzoate (top) and 4-benzoyloxy-2,2′-dimethyl-6,6′-dinitrobiphenyl (bottom) as a function of the torsional angles defined by C-6, C-1, O, C(O) and C-5, C-4, O, C(O), respectively.

polarization that is a function of the energy difference between any two rotational states of the biphenyl core contributing opposite dipole moments along the S_C* polar axis (i.e., transverse to the molecular long axis). The calculated energy profiles (AM1)[14] for rotation about the ester C−O bonds of 3-methyl-5-nitrophenyl benzoate (**11**) and 4-benzoyloxy-2,2′-dimethyl-6,6′-dinitrobiphenyl (**12**) are used to model the intramolecular rotation of the biphenyl core in (−)-**1** (Figure 6).[15] Both profiles suggest a small energetic bias for intramolecular rotation of the biphenyl core in the S_C binding site, which is consistent with the low polarization power exhibited by (−)-**1** in the S_C host **PhBz**. The energy profile calculated for **11** shows two pairs of symmetry-related minima **a**, **a′** and **b**, **b′** ($\Delta H^o = 0.4$ kcal/mol). On the time average, these minima correspond to the planar conformations **I** and **II**, respectively, which have opposite transverse dipole moments; AM1 calculations give dipole moment values of 4.0 D (**I**) and 5.3 D (**II**) along the vectors shown in Figure 5. When the atropisomeric biphenyl group is included, rotational symmetry about the ester C−O bond is completely broken, as shown by the energy profile calculated for **12**, with the global minimum corresponding to a conformation in which the ester carbonyl group is oriented away from both nitro substituents.

The results showing the polarization power of (−)-**1** in **NCB76** to be eight times that estimated as the upper limit in **PhBz** can be correlated to the difference in dielectric anisotropy of the two hosts: **NCB76** has a large transverse dipole moment and exhibits a negative dielectric anisotropy ($\epsilon\| - \epsilon\perp$) that is ca. 10 times that of **PhBz**.[1c] This suggests that the amplification of P_S in **NCB76** is a manifestation of induced polar ordering of the S_C host via transverse dipole−dipole coupling with (−)-**1**. Along with polar ordering of the host, it is likely that transverse dipole−dipole coupling between (−)-**1** and **NCB76**

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(15) It is assumed that the 2,2′-dimethyl-6,6′-dinitrobiphenyl group is conformationally rigid. The calculated energy profile (AM1) for 360° rotation about the central bond of the atropisomeric biphenyl is steep and shows a single pair of symmetry-related energy minima at dihedral angles approaching 90° and 270°, with a rotational barrier of ca. 35 kcal/mol.

causes a significant asymmetric distortion of the achiral S_C binding site, which can further contribute to rotational ordering of the dopant. Such distortion is also likely to affect the global conformational minimum of the dopant, which ultimately controls the orientation of the core with respect to the polar axis, thus providing a possible explanation for the observed sign inversion of P_S. Another contributing factor to the sign inversion may be a shift in the conformational equilibrium of the biphenyl core toward conformations predicted to be of higher energy in the gas phase (e.g., **II**). These conformations have larger transverse dipole moments and should therefore be stabilized to a greater extent by a S_C host with high negative dielectric anisotropy.

In summary, we have demonstrated for the first time the induction of a ferroelectric S_C* phase by a dopant with an atropisomeric biphenyl core as stereopolar unit.[16] The polarization power and sign of polarization induced by (−)-**1** showed a dependence on the nature of the S_C host that is consistent with the behavior of Type II dopants first reported by Stegemeyer.[8a] The > 8-fold enhancement in polarization power resulting from the change in S_C host is one of the largest thus far reported for a Type II dopant. Combined with the observed deviation from linearity of the P_o (x_d) function over a relatively narrow x_d range, these results suggest that the polarization power of (−)-**1** is remarkably sensitive to the environment of the dopant, which may be due to the unusual conformational mobility of the stereopolar unit in (−)-**1**. Further work aimed at probing the generality of this phenomenon in a wider variety of S_C hosts and at enhancing the rotational order of the biphenyl core to produce dopants with higher δ_p values is in progress.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ACF-200 and AM-400 NMR spectrometers in deuterated chloroform and deuterated DMSO. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low-resolution EI mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer; peaks are reported as *m*/*z* (% intensity relative to the base peak). High-resolution EI mass spectra were performed by the University of Ottawa Regional Mass Spectrometry Center. Optical rotations were measured on a Perkin-Elmer 241 polarimeter at room temperature. Differential scanning calorimetry measurements were carried out using a Perkin-Elmer DSC-7 instrument. Elemental analyses were performed by Guelph Chemical Laboratories Ltd (Guelph, Ontario) and by MHW Laboratories (Phoenix, AZ). Melting points were measured on a Mel-Temp II melting point apparatus and are uncorrected.

Materials. All reagents were obtained from commercial sources and used without further purification unless otherwise noted. Dimethylformamide (DMF) was distilled from BaO under reduced pressure and stored over molecular sieves. Hexamethylphosphoramide (HMPA) was distilled from CaH_2 under N_2. Methylene chloride (CH_2Cl_2) was distilled from P_2O_5 under N_2. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under N_2. 4-Methoxy-2-nitroaniline (**2**) was purchased from Aldrich. The S_C host **PhBz** was prepared as a racemic mixture according to the published procedure[17] and recrystallized twice from hexanes. The S_C host **NCB76** was provided by Prof. H. Stegemeyer.

4-Methoxy-2-nitroisonitrosoacetanilide (3). A suspension of **2** (50 g, 300 mmol) in 2 M aqueous HCl (100 mL) was added to a solution of chloral hydrate (59 g, 360 mmol), $NH_2OH\cdot HCl$ (74 g, 1.07 mol) and anhydrous Na_2SO_4 (426 g, 3 mol) in 2 L of H_2O preheated to 55 °C. The mixture was stirred mechanically at 55 °C overnight and then allowed to cool to room temperature. The precipitated product was collected by filtration, washed with H_2O, and dried in a vacuum oven to give 67 g (93%) of **3** as an orange solid: mp 102−104 °C; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 3.83 (s, 3H), 7.37 (dd, $J = 3.0$ Hz, $J = 9.1$ Hz, 1H), 7.58 (d, $J = 3.5$ Hz, 1H), 7.59 (s, 1H), 8.05 (d, $J = 9.1$ Hz, 1H), 10.62 (s, 1H), 12.49 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 56.0, 109.1, 121.5, 125.1, 125.6, 140.8, 143.3, 155.6, 160.6; MS (EI) *m*/*z* 239 (M^+, 16), 193 (34), 176 (15), 168 (100), 153 (38), 150 (10), 133 (8), 122 (48), 120 (37), 107 (32); HRMS (EI) calcd for $C_9H_9N_3O_5$: 239.0542. Found: 239.0524.

5-Methoxy-7-nitroisatin (4). Compound **3** (67 g, 280 mmol) was carefully added in small portion to a stirred solution of concentrated H_2SO_4 (250 mL) preheated to 90 °C. The temperature was kept below 105 °C throughout the addition. The resulting dark solution was stirred for an additional 15 min, then cooled to 60 °C, and poured onto 200 g of crushed ice. The precipitated product was collected by filtration, washed with H_2O, and dried in a vacuum oven to give 51.5 g (83%) of **4** as an orange powder: mp 236−238 °C; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 3.86 (s, 3H), 7.58 (d, $J = 1.9$ Hz, 1H), 7.73 (d, $J = 1.9$ Hz, 1H), 11.54 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 56.5, 113.8, 118.3, 122.3, 131.9, 138.7, 154.3, 160.0, 181.6; MS (EI) *m*/*z* 222 (100), 205 (99), 194 (43), 175 (72), 164 (34), 147 (36), 132 (25), 120 (9), 116 (8), 104 (72), 93 (64); HRMS (EI) calcd for $C_9H_6N_2O_5$: 222.0277. Found: 222.0279.

Methyl 2-Iodo-5-methoxy-3-nitrobenzoate (5). A 30% H_2O_2 solution (15 mL) was added dropwise to a stirred solution of **4** (14.5 g, 65 mmol) in 50 mL of 2 M aqueous NaOH cooled in an ice/H_2O bath. The mixture was stirred at room temperature overnight and then carefully acidified with 10 mL of glacial AcOH. The solid precipitate was collected by filtration, washed with H_2O, and dried in a vacuum oven to give 9.7 g of crude 2-amino-5-methoxy-3-nitrobenzoic acid as a brown solid. The crude product was dissolved in concentrated H_2SO_4 (40 mL) and cooled to 5 °C, and 4.6 g of $NaNO_2$ (67 mmol) was slowly added while maintaining the temperature below 10 °C. The mixture was diluted with 85% H_3PO_4 (80 mL), stirred at 5 °C for 1 h, and then poured onto 350 g of crushed ice. A solution of KI (11.2 g, 67 mmol) in H_2O (30 mL) was slowly added, and the mixture was stirred at room temperature overnight. The solid precipitate was collected by filtration, dissolved in 10% aqueous NaOH, and treated with activated charcoal while heating over a steam bath. After cooling, the mixture was filtered and acidified with 12 M aqueous HCl. The resulting light brown precipitate was collected by filtration, washed with H_2O, and dried in a vacuum oven to give 11.2 g of 2-iodo-5-methoxy-3-nitrobenzoic acid as a tan solid: ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 3.86 (s, 3H), 7.37 (d, $J = 2.9$ Hz, 1H), 7.62 (d, $J = 2.9$ Hz, 1H). The crude product was taken up in a mixture of MeOH (275 mL) and concentrated H_2SO_4 (30 mL) and refluxed with stirring for 12 h. After cooling, the mixture was poured into H_2O and extracted with CH_2Cl_2 (3 × 200 mL). The combined extracts were washed with H_2O, dried ($MgSO_4$), and concentrated to an orange solid, which was recrystallized from EtOH to give 10.2 g (46%) of **5** as bright orange crystals: mp 61−62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.98 (s, 3H), 7.26 (d, $J = 3.0$ Hz, 1H), 7.32 (d, $J = 3.0$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 53.1, 56.3, 73.1, 112.2, 118.6, 140.8, 156.4, 159.9, 166.6; MS (EI) *m*/*z* 337 (M^+, 100), 321 (10), 306 (33), 291 (20), 276 (31), 260 (9), 248 (12), 233 (22), 218 (12), 205 (12), 189 (9), 180 (14), 165 (12), 149 (82), 142 (38), 133 (20), 127 (37), 121 (11), 105 (64). Anal. Calcd for $C_9H_8INO_5$: C, 32.07; H, 2.39; N, 4.16; I, 37.65. Found: C, 32.46; H, 2.36; N, 4.09; I, 37.26.

(±)-Dimethyl 4,4′-Dimethoxy-6,6′-dinitrobiphenyl-2,2′-dicarboxylate (6). A mixture of **5** (2.88 g, 8.5 mmol) and Cu bronze (2.71 g, 43 mmol) in 50 mL of dry DMF was refluxed with stirring under N_2 overnight. After cooling, the mixture was diluted with benzene (50 mL), washed twice with 2 M aqueous HCl, dried ($MgSO_4$), and concentrated to give an orange solid. Purification by flash chromatography on silica gel (40% EtOAc/hexane) gave 1.28 g (72%) of pure **6** as a yellow solid: mp 139−140 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ

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(16) Atropisomeric dopants have been reported on several occasions to induce a cholesteric phase in nematic liquid crystal hosts. For recent examples, see: (a) Gottarelli, G.; Proni, G.; Spada, G. P.; Fabbri, D.; Gladiali, S.; Rosini, C. *J. Org. Chem.* **1996**, *61*, 2013, and references cited therein. (b) Bhatt, J. C.; Keast, S. S.; Neubert, M. E.; Petschek, R. G. *Liq. Cryst.* **1995**, *18*, 367. (c) Zhang, M.; Schuster, G. B. *J. Phys. Chem.* **1992**, *96*, 3063.

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(19) Wavefunction, Inc., 18401 Von Karmann, #210, Irvine, CA.

3.66 (s, 6H), 3.96 (s, 6H), 7.77−7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 56.1, 113.1, 120.8, 124.2, 132.3, 150.0, 159.0, 165.1; MS (EI) *m/z* 420 (M^+, 5), 374 (97), 342 (31), 313 (100), 298 (72), 283 (32), 267 (11), 255 (21), 241 (8), 227 (16), 212 (12), 199 (11), 184 (14), 156 (13). Anal. Calcd for $C_{18}H_{16}N_2O_{10}$: C, 51.44; H, 3.84; N, 6.66. Found: C, 51.33; H, 4.00; N, 6.72.

(±)-4,4′-Dimethoxy-6,6′-dinitrobiphenyl-2,2′-dicarboxylic Acid (7). A mixture of **6** (2.3 g, 5.5 mmol) and NaOH (1.04 g, 26 mmol) in 100 mL of 3:2 EtOH/H_2O was refluxed with stirring overnight. After cooling, the EtOH was removed in vacuo, and the aqueousueous phase was acidified with 2 M aqueous HCl and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with H_2O and brine, dried ($MgSO_4$), and concentrated to give 2.1 g (98%) of **7** as a yellow solid: mp 252−254 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 3.93 (s, 6H), 7.69 (d, $J = 2.7$ Hz, 2H), 7.83 (d, $J = 2.7$ Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 56.3, 112.2, 119.8, 122.6, 134.1, 150.1, 158.7, 165.8; MS (EI) *m/z* 392 (M^+, 3), 374 (1), 360 (10), 346 (8), 330 (13), 316 (14), 298 (100), 283 (60), 270 (34), 254 (61), 241 (21), 239 (27), 226 (38), 211 (34), 199 (24), 183 (31), 171 (21), 156 (14), 140 (28). Anal. Calcd for $C_{16}H_{12}O_{10}N_2$: C, 48.99; H, 3.08; N, 7.14. Found: C, 49.23; H, 3.00; N, 7.11.

(±)-2,2′-Bis(bromomethyl)-4,4′-dimethoxy-6,6′-dinitrobiphenyl (9). To a stirred solution of **7** (1.8 g, 4.6 mmol) in 40 mL of dry THF cooled to 0 °C was added dropwise 20 mL of BH_3•THF (1M solution). The mixture was then allowed to warm to room temperature and stirred for 20 h. The reaction was carefully quenched by slow addition of H_2O (100 mL) and extracted with EtOAc (3 × 50 mL). The organic extracts were combined and concentrated to an oily residue. The residue was taken up in EtOAc (50 mL), washed with H_2O (2×) and brine, dried ($MgSO_4$), and concentrated to give 1.5 g of the diol **8** as a yellow solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.89 (s, 6H), 4.04 (d, $J = 13.4$ Hz, 2H), 4.19 (d, $J = 13.4$ Hz, 2H), 7.31 (d, $J = 2.5$ Hz, 2H), 7.48 (d, $J = 2.5$ Hz, 2H). The crude **8** was taken up in a mixture of 48% aqueous HBr (30 mL) and glacial AcOH (20 mL) and refluxed with stirring for 24 h. After cooling, the mixture was poured into H_2O and extracted with EtOAc (3 × 50 mL), the combined extracts were washed with H_2O, dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (5% isopropanol/hexanes) gave 1.16 g (51%) of **9** as a yellow solid: mp 215−217 °C; ^{1} H NMR (200 MHz, acetone-d_6) δ 4.20 (d, $J = 12$ Hz, 2H), 4.36 (d, $J = 12$ Hz, 2H), 7.51 (d, $J = 2.6$ Hz, 2H), 7.70 (d, $J = 2.6$ Hz, 2H), 9.68 (s, 2 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 31.2, 111.8, 119.6, 123.1, 139.4, 149.1, 158.0; MS (EI) 464 (M+4, 4), 462 (M+2, 9), 460 (M+, 4), 418 (4), 416 (8), 414 (4), 383 (5), 381 (5), 337 (24), 335 (26), 271 (62), 256 (99), 239 (100), 226 (49), 212 (47), 197 (48), 181 (43), 167 (33), 152 (75), 149 (93), 139 (57), 127 (38), 115 (75); HRMS (EI) calcd for $C_{14}H_{10}N_2O_6Br_2$: 459.8910. Found: 459.8914.

(±)-4,4′-Dihydroxy-2,2′-dimethyl-6,6′-dinitrobiphenyl (10). A mixture of **9** (2.31 g, 5 mmol) and $NaBH_3CN$ (3.2 g, 51 mmol) in 20 mL of dry HMPA was stirred at 55 °C for 20 h under N_2. After cooling, the mixture was poured carefully into 2 M aqueous HCl and extracted with EtOAc (3 × 50 mL). The combined extracts were washed with 2 M aqueous HCl, dried ($MgSO_4$), and concentrated. The residue was purified by flash chromatography on silica gel (40% EtOAc/hexanes) to give 1.16 g (76%) of **10** as a yellow solid: mp 214−215 °C (dec); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.96 (s, 6H), 5.28 (br s, 2 H), 7.06 (d, $J = 2.5$ Hz, 2H), 7.41 (d, $J = 2.5$ Hz, 2H); ^{13}C NMR (50 MHz, DMSO-d_6) δ 19.5, 108.2, 120.4, 121.9, 140.3, 149.2, 157.2; MS (EI) *m/z* 304 (M^+, 100), 258 (56), 242 (19), 240 (20), 230 (29), 228 (80), 216 (45), 214 (43), 202 (30), 190 (44), 188 (43), 184 (36), 174 (28), 160 (32), 152 (44), 147 (29), 139 (41), 128 (65), 115 (90). Anal. Calcd for $C_{14}H_{12}N_2O_6$: C, 55.27; H, 3.98; N, 9.21. Found: C, 55.42; H, 4.06; N, 8.99.

(−)-2,2′-Dimethyl-6,6′-dinitro-4,4′-bis[(4-*n*-octyloxybenzoyl)oxy]-biphenyl ((−)-1). Under a N_2 atmosphere, 82 mg (0.4 mmol) of solid DCC was added to a solution of **10** (50 mg, 0.16 mmol), 4-*n*-octyloxybenzoic acid (100 mg, 0.4 mmol), and DMAP (50 mg, 0.4 mmol) in 10 mL of dry CH_2Cl_2. The mixture was stirred at room temperature for 24 h and then filtered. The filtrate was eluted through a short silica gel column with CH_2Cl_2 to give 110 mg (89%) of (±)-**1** as a white solid. The product was resolved by chiral stationary phase HPLC using a semiprep (*S*,*S*)-Whelk-O 1 column (40:3:1 hexanes/isopropyl alcohol/CH_2Cl_2, 3 mL/min) and recrystallized twice from hexanes to give (−)-**1** in optically pure form: mp 130−132 °C; $[\alpha]_D = -5.01$ (*c* 0.5, CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, $J = 6.7$ Hz, 6H), 1.26−1.55 (m, 20 H), 1.76−1.92 (m, 4H), 2.06 (s, 6H), 4.06 (t, $J = 6.5$ Hz, 4 H), 7.01 (d, $J = 8.9$ Hz, 4H), 7.52 (d, $J = 2.4$ Hz, 2H), 7.93 (d, $J = 2.4$ Hz, 2H), 8.14 (d, $J = 8.9$ Hz, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 20.2, 22.6, 26.0, 29.0, 29.2, 29.3, 31.8, 68.4, 114.5, 116.3, 120.5, 128.1, 128.6, 132.5, 139.9, 148.5, 150.6, 163.9, 164.0. Anal. Calcd for $C_{44}H_{52}N_2O_{10}$: C, 68.73; H, 6.82; N, 3.64. Found: C, 68.49; H, 6.74; N, 3.58.

Ferroelectric Measurements. Texture analyses and transition temperature measurements for the doped liquid crystal mixtures were carried out using a Nikon Labophot-2 polarizing microscope fitted with a Instec HS1-i hot stage. Spontaneous polarization (P_S) values were measured as a function of temperature by the triangular wave method[18] (6 V/μm, 60−80 Hz) using a Displaytech APT II polarization testbed in conjunction with the Instec hot stage. For each data point taken, the temperature of the sample was allowed to fully equilibrate in order to rule out any temperature effect during measurement. Polyimide-coated ITO glass cells (4 μm × 0.25 cm^2) supplied by Displaytech Inc. were used for all the measurements. Good alignment was obtained by slow cooling of the filled cells from the isotropic phase via the chiral nematic and S_A* phases. Tilt angles (θ) were measured as a function of temperature between crossed polarizers as half the rotation between two extinction positions corresponding to opposite polarization orientations. The sign of P_S along the polar axis was assigned from the relative configuration of the electrical field and the switching position of the sample according to the established convention.[4]

Calculations. All calculations were carried out at the semiempirical AM1 level[14] using Spartan version 3.0.1.[19] Rotational energy profiles of the ester linkages in **11** and **12** were obtained by constraining the torsional angles defined by C-6, C-1, O, C(O) and C-5, C-4, O, C(O), respectively, and performing a full geometry optimization on the rest of the molecules. All minima were determined by full geometry optimization and confirmed as minima by vibrational analysis.

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