Electronic Supplementary Information for:

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

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1. EXPERIMENTAL

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers; chemical shifts are reported in δ (ppm) relative to tetramethylsilane. Low-resolution mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer or an Applied Biosystems/MDS Sciex QSTAR XL QqTOF mass spectrometer. Peaks are reported as *m/z* (percent intensity relative to the base peak). High resolution EI mass spectra were recorded on a Waters/Micromass GCT mass spectrometer, and high resolution ESI mass spectra were recorded on an Applied Biosystems/MDS Sciex QSTAR XL QqTOF mass spectrometer. Preparative chiral stationary phase HPLC separations were performed using a Daicel Chiralpak AS column (50 cm x 5 cm i.d.). Circular dichroism spectra were recorded on a Jasco J-715 spectropolarimeter in hexanes (spectro grade). Variable temperature X-ray diffraction measurements were performed at the Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM) of Université Laval using a Siemens/Bruker Kristalloflex 760 diffractometer fitted with a Hi-Star bidimensional detector (Cu Kα radiation, λ = 1.5418 Δ). Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. UV-Vis spectra were recorded on a Varian Cary 3 UV-Vis spectrometer. Differential scanning calorimetry analyses was performed on a Perkin-Elmer DSC-7 instrument with a scanning rate of 5 K/min. Flash chromatography was performed using 60 Å silica gel (Silicycle Inc., Quebec) as the adsorbent. All final dopant molecules were recrystalized from HPLC grade hexanes after being passed through a 0.45μm PTFE membrane. Phase transitions of doped liquid crystal mixtures were determined on cooling from the isotropic liquid phase based on changes in textures when viewed as thin films in either 4 μm rubbed polyimide-coated ITO glass cells (E.H.C. Co., Japan), or on untreated glass slides with a cover slip, using either a Nikon Eclipse E600 POL or Labophot-2 POL polarized microscope fitted with a Linkam LTS 350 hot stage.

Materials

All reagents, materials, and the liquid crystal hosts **PhP** and **NCB76** were obtained from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon, or eluted through two columns containing activated alumina and copper using a PureSolv 400 solvent purification system (Innovative Technology Inc., Massachusetts). The liquid crystal hosts **PhB** and **DFT**, and (*RS*)-dimethyl 6,6'-dimethyl-4,4'-dinitro[1,1'-biphenyl]-2,2'-dicarboxylate ((*RS*)-**7**) were synthesized according to literature procedures and shown to have the expected physical and spectral properties.[1-3]

(*RS*)-6,6'-Dimethyl-4,4'-dinitro[1,1'-biphenyl]-2,2'-dicarboxylic acid ((*RS*)-8). A suspension of (*RS*)-**7** (2.64 g, 6.80 mmol) in a 1:1 solution of 0.5 M NaOH/EtOH (100 mL) was heated to reflux for 20

min with stirring. The reaction mixture was cooled to room temperature, acidified with conc. HCl and extracted with ether (3 × 60 mL). The organic layers were washed with brine, dried ($MgSO_4$) and concentrated to give 2.31 g (94%) of (*RS*)-**8** as a pale yellow solid: mp 184-185 °C; ^{1}H NMR (200 MHz, DMSO-*d*$_6$) δ 8.55 (d, *J* = 2.6 Hz, 2H), 8.43 (d, *J* = 2.6 Hz, 2H), 1.94 (s, 6H).
Anal. Calcd. for $C_{16}H_{12}N_2O_8$: C, 53.34; H, 3.36; N, 7.78. Found: C, 53.59; H, 3.60; N, 7.60.

(*RS*)-2,2'-Bis(hydroxymethyl)-6,6'-dimethyl-4,4'-dinitro[1,1'-biphenyl] ((*RS*)-9). To a solution of (*RS*)-**8** (0.97 g 2.69 mmol) in THF (5 mL) cooled to 0 °C under an argon atmosphere was added dropwise a solution of BH_3•THF (1 M in THF). The solution was stirred overnight while warming to room temp, and the excess BH_3•THF was quenched with a 1:1 THF/H_2O (10 mL) solution. The aqueous layer was saturated with K_2CO_3 and the organic layer separated. The aqueous layer was extracted with THF (2 × 25 mL), the organic layers were combined and concentrated. The residue was taken up in EtOAc and washed with H_2O, brine, dried ($MgSO_4$), and concentrated to give 0.74 g (83%) of (*RS*)-**9** as a yellow solid: mp 201-204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 2H), 8.16 (s, 2H), 4.36 (d, 2H, *J* = 12 Hz), 4.16 (d, 2H, *J* = 12 Hz), 1.99 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 19.8, 61.9, 121.9, 124.3, 137.6, 139.7, 142.4, 147.9.

(*RS*)-2,2'-Bis(bromomethyl)-6,6'-dimethyl-4,4'-dinitro[1,1'-biphenyl] ((*RS*)-10). To a solution of (*RS*)-**9** (0.33 g, 1.0 mmol) and CBr_4 (1.66 g, 5.0 mmol) in CH_2Cl_2 (30 mL) cooled to 0 °C under an argon atmosphere was added portion-wise a solution of PPh_3 (1.05 g, 4.0 mmol) in CH_2Cl_2 (15 mL).[4] The reaction was stirred at room temp for 48 hrs, then concentrated and the crude product purified by flash chromatography on silica gel (3:1 hexanes/EtOAc) to give 0.38 g (78%) of (*RS*)-**10** as a white solid: mp 259-261 °C; ^{1}H NMR (300 MHz, $CDCl_3$), δ 8.33 (d, 2H, *J* = 3 Hz), 8.18 (d, 2H, *J* = 3 Hz), 4.14 (d, 2H, *J* = 9 Hz), 4.07 (d, 2H, *J* = 9 Hz), 2.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 29.5, 123.9, 125.3, 137.3, 138.9, 142.2, 148.3; MS (EI) *m/z* 460 (M+2, <1), 458 (M+, <1), 456 (M–2, <1), 444 (1), 442 (4), 440 (1), 379 (100), 377 (100), 333 (100), 331 (100), 297 (99), 253 (99), 252 (100), 251 (85), 238 (31), 237 (19), 236 (18), 235 (21), 222 (19), 207 (34), 206 (100), 205 (86), 204 (50), 203 (46), 202 (56), 192 (54), 191 (98), 190 (97), 189 (100), 179 (78), 178 (92), 177 (30), 176 (57), 165 (89), 163 (26), 153 (13), 152 (67), 151 (24), 139 (23), 115 (26); HRMS (EI) Calcd for $C_{16}H_{14}N_2O_4Br_2$: 455.9320. Found: 455.9323.

(*RS*)-1,11-Dimethyl-3,9-dinitro-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*RS*)-11). A mixture of (*RS*)-**10** (0.36 g, 0.79 mmol) and Na_2S•$9H_2O$ (0.57 g, 2.4 mmol) in 9:1 EtOH/H_2O (150 mL) was heated at reflux overnight. Upon cooling to room temp, the EtOH was removed *in vacuo* and the residue dissolved in EtOAc. The organic layer was washed with H_2O (3 × 50 mL), brine, dried ($MgSO_4$) and concentrated to give 0.25 g of (*RS*)-**11** as an orange solid, which was used in the next step without further purification.

(*RS*)-3,9-Diamino-1,11-dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*RS*)-12). A mixture of (*RS*)-**11** (0.25 g, 0.76 mmol) and $SnCl_2$•$2H_2O$ (2.06 g, 9.1 mmol) in EtOH (40 mL) was heated at reflux overnight.[5] Upon cooling to room temperature the reaction mixture was diluted with H_2O (150 mL), neutralized with NaOH (aq) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with H_2O (2×), brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (3:1 hexane/EtOAc) gave 0.12 g (58% over the 2 steps) of (*RS*)-**12** as a white solid; mp 234-236 °C; ^{1}H NMR (300 MHz, acetone-*d*$_6$), δ 6.53 (d, 2H, *J* = 3 Hz), 6.45 (d, 2H, *J* = 3 Hz), 4.49 (broad s, 4H), 3.20, (d, 2H, *J* = 12 Hz), 3.08 (d, 2H, *J* = 12 Hz), 1.94 (s, 6H); ^{13}C NMR (100 MHz, acetone-*d*$_6$), δ 20.0, 32.8, 112.2, 115.7, 127.7, 137.3, 137.5, 148.4; MS (EI) *m/z* 270 (M^+, 100), 237 (33), 222 (86); HRMS (EI) Calcd for $C_{16}H_{18}N_2S$: 270.1191. Found: 270.1197.

(–)-(*R*)- and (+)-(*S*)-3,9-Dihydroxy-1,11-dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*R*)- and (*S*)-13). To a solution of (*RS*)-**12** (0.316 g, 1.17 mmol) in 10% aq H_2SO_4 (25 mL) cooled to 0 °C was added dropwise a solution of $NaNO_2$ (0.177, 2.57 mmol) in H_2O (3 mL). After stirring for 15 min at 0 °C, then 15 min at room temperature, the solution was added dropwise to a 10% aq H_2SO_4 solution (75 mL) heated to reflux. After refluxing overnight, the solution was cooled, poured into H_2O and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (1:1 hexane/EtOAc) gave 180 mg (56%) of (*RS*)-**13** as a white solid: mp 234-236 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 8.23, (s, 2H), 6.72 (d, 2H, *J* = 3 Hz), 6.65, (d, 2H, *J* = 3 Hz), 3.19, (m, 4H), 1.99, (s, 6H); ^{13}C NMR (acetone-d_6 100 MHz), δ 19.9, 32.5, 112.9, 116.4, 129.9, 138.0, 138.2, 157.5; LRMS (EI) *m/z* 272 (M^+, 100), 239 (68), 224 (80), 221 (15), 211 (25), 195 (11), 181 (13), 165 (13); HRMS (EI) Calcd for $C_{16}H_{16}O_2S$: 272.0877. Found: 272.0871. Resolution by chiral phase HPLC (Daicel Chiralpak AS column, 50 cm × 5 cm i.d., 90:10 hexanes/EtOH, 50 mL/min) gave 62 mg of (*R*)-**13** (first eluant), > 99% ee, $[\alpha]_D$ –222 (c = 0.045, acetone) and 52 mg of (*S*)-**13** (second eluant), 86% ee.

(–)-(*R*)-3,9-Bis[(4-butoxybenzoyl)oxy]-1,11-dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*R*)-5b). A solution of (*R*)-**13** (17 mg, 0.062 mmol, > 99% ee), 4-butoxybenzoic acid (61 mg, 0.32 mmol), DCC (64 mg, 0.32 mmol) and DMAP (39 mg, 0.32 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature under an argon atmosphere overnight. The reaction mixture was filtered and concentrated. Purification by flash chromatography on silica gel (6:1 hexanes/EtOAc) gave 23 mg (60%) of (*R*)-**5b** as a white solid: mp 175-176 °C; $[\alpha]_D$ –65 (c = 0.09, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, 2H, *J* = 8 Hz), 7.11 (s, 2H), 7.05 (s, 1H), 6.98 (d, 2H, *J* = 8 Hz), 4.05, (m, 4H), 3.31 (m, 4H), 2.14 (s, 6H), 1.81 (m, 4H), 1.45-1.60 (m, 4H), 0.95-1.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.2, 19.8, 31.1, 32.0, 68.0, 114.3, 118.5, 121.5, 122.2, 132.2, 134.4, 136.9, 137.8, 150.7, 163.6, 164.9; MS (EI) *m/z* 624 (M+, 5), 177 (100), 121 (33); HRMS (EI) Calcd for $C_{38}H_{40}O_2S$: 624.2546. Found: 624.2525.

(–)-(*R*)-1,11-Dimethyl-3,9-bis[(4-octyloxybenzoyl)oxy]-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*R*)-5c). The procedure used for the synthesis of (*R*)-**5b** was repeated with (*R*)-**13** (25 mg, 0.092 mmol, > 99% ee), 4-octyloxybenzoic acid (117 mg, 0.47 mmol), DCC (96 mg, 0.47 mmol) and DMAP (59 mg, 0.47 mmol). Purification by flash chromatography on silica gel (9:1 hexanes/EtOAc) gave 45 mg (66%) of (*R*)-**5c** as a white solid: mp 116-117 °C; $[\alpha]_D$ –50 (c = 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, 4H, *J* = 8 Hz), 7.11 (s, 2H), 7.05 (s, 2H), 6.98 (d, 4H, *J* = 8 Hz), 4.04 (t, 4H, *J* = 8 Hz), 3.31 (m, 4H), 2.14 (s, 6H), 1.82 (m, 4H), 1.20-1.55 (m, 20H), 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.8, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3, 114.3, 118.6, 121.5, 122.2, 132.3, 134.4, 136.9, 137.8, 150.7, 163.6, 164.9; MS (EI), *m/z* 736 (M+, 1), 233 (100); HRMS (EI) Calcd for $C_{46}H_{56}O_6S$: 736.3798. Found: 736.3815.

(+)-(*S*)-3,9-Dihydroxy-1,11-dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*S*)-13) via classical resolution of the diacid (*RS*)-8.[5] To a solution of (*RS*)-**8** (1.81 g, 5.02 mmol) in acetone (25 mL) was added quinine (1.81 g, 5.02 mmol). The mixture was refluxed for 30 min, then cooled to room temperature and the precipitated salt was collected by filtration, washed once with cold acetone and dried under vacuum. The salt (1.71 g) was decomposed in 4 M aq HCl (10 mL) and the diacid extracted with ether (3 × 10 mL). The combined extracts were dried ($MgSO_4$) and concentrated to give 594 mg (33%) of (*S*)-**8**: mp 187-191 °C; $[\alpha]_D$ +2.5° (c = 1.7, MeOH). A small sample of the resolved diacid was converted to the diester (*S*)-**7** by treatment with MeI and K_2CO_3 in refluxing acetone, and the enantiomeric excess of the diester (> 95%) was determined by ^{1}H NMR spectroscopy ($CDCl_3$) in the presence of the chiral shift reagent europium tris[3-(heptafluoropropyhydroxymethylene)-(+)-camphorate] (3:1 reagent/diester). The resolved diacid (*S*)-**8** was converted to (*S*)-**13** following the route described for the synthesis of (*RS*)-**13**: $[\alpha]_D$ +392 (c = 0.1, MeOH)

(+)-(*S*)-3,9-Bis[4-(dodecyloxybenzoyl)oxy]-1,11-dimethyl-5,7-dihydrodibenzo[*c*,*e*]thiepin ((*S*)-5a). The procedure used for the synthesis of (*R*)-**5b** was repeated with (*S*)-**13** (18.2 mg, 0.066 mmol, > 95% ee), 4-dodecyloxybenzoic acid (51.0 mg, 0.17 mmol), DCC (34.1 mg, 0.17 mmol) and DMAP (20.8 mg, 0.17 mmol). Purification by flash chromatography on silica gel (12:1 hexanes/EtOAc) gave 25.6 mg, (45%) of (*S*)-**5a** as a white solid: mp 111-113 °C; $[\alpha]_D$ +99 (c = 0.02, acetone); ^{1}H NMR (400 MHz $CDCl_3$), δ 8.14 (d, 4H, J = 8 Hz), 7.11 (s, 2H), 7.04 (s, 2H), 6.97 (d, 4H, J = 8 Hz), 4.04 (t, 4H, J = 8 Hz), 3.31 (m, 4H), 2.14 (s, 6H), 1.82 (m, 4H), 1.20-1.55 (m, 36H), 0.88 (t, 6H, J = 8Hz); ^{13}C NMR ($CDCl_3$ 100 MHz) δ 14.1, 19.8, 22.7, 26.0, 29.1, 29.3, 29.6, 29.6, 31. 9, 32.0, 68.3, 114.3, 118.5, 121.5, 122.2, 132.2, 134.4, 136.9, 137. 8, 150.7, 163.6, 164.8; MS (EI) *m/z* 848 (M+, 64), 560 (95), 503 (20), 429 (76), 415 (30), 401 (18), 369 (15), 355 (100); HRMS (EI) Calcd for $C_{54}H_{72}O_6S$: 848.5050. Found: 848.5067.

Ferroelectric Polarization Measurements

Sample Preparation. Samples for ferroelectric measurements were loaded by capillary action into polyimide-coated ITO glass cells supplied by E.H.C. Co. (4 µm spacing, 0.16 cm^2 addressed area). The cell thickness was determined by the capacitance of an empty cell using a Displaytech APT-III polarization testbed (Displaytech Inc. Longmont, CO). Each cell was heated to the isotropic liquid phase under an AC triangular wave (100 Hz, 6V/µm) to remove air bubbles in the electrically addressed area. Good alignment of the liquid crystal mixtures was achieved by slow cooling from isotropic to the SmC* phase (0.5-2 K/min).

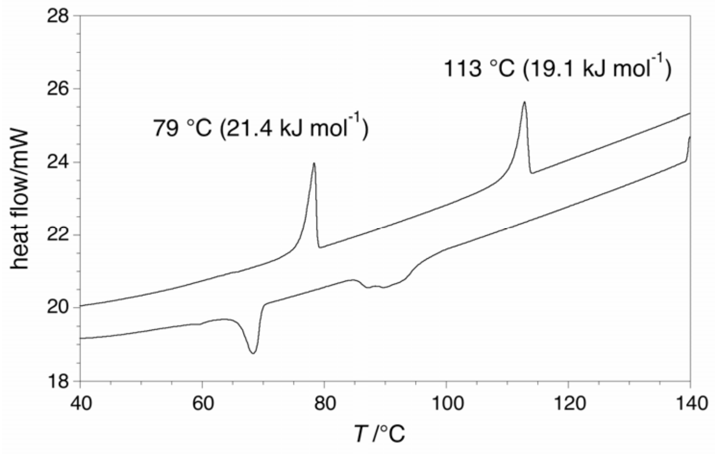
Polarization Measurements. Spontaneous polarizations P_s were measured using the triangular wave method (100 Hz, 6 V/µm).[6] Tilt angles θ were measured by polarized microscopy as half the rotation between the two extinction positions corresponding to opposite polarization directions. The sign of P_s along the polar axis was assigned from the relative configuration of the electric field and the switching position of the sample according to the established convention.[7] Reduced polarizations P_o were calculated for each mixture at $T\text{-}T_C$ = -5 K.

Helical Pitch Measurements

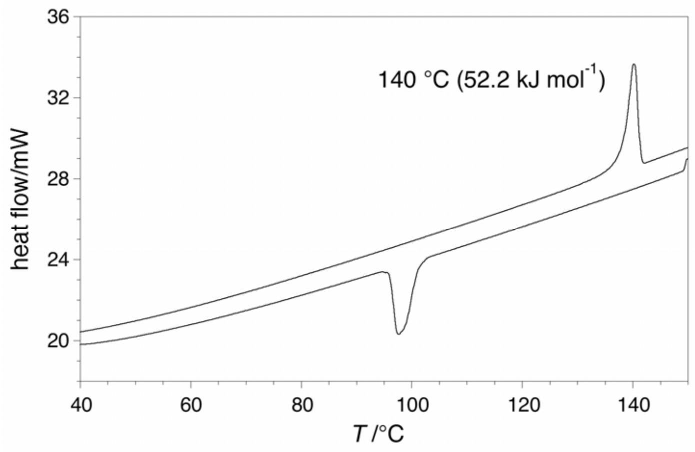
Samples for helical pitch measurements were loaded by capillary action into wedge glass cells supplied by E.H.C. Co. (tanθ = 0.14). Grandjean textures were obtained by slow cooling from isotropic to the N* phase (0.5-2.0 K/min). Pitch measurements were taken over a range of temperatures ($T\text{-}T_{N\text{-}I}$ = –0.5 to –10 K). At each temperature, the sample was allowed to equilibrate for 10 minutes before being photographed. The value of *s* for each sample was determined by measuring the distance between two non-adjacent dark lines (*d*) and dividing by the number of Grandjean steps (*n*) separating these two lines (i.e., *s* = *d/n*). This was repeated three times using different areas of the sample.

2. DSC traces

a) (*S*)-**5a**, 100% ee



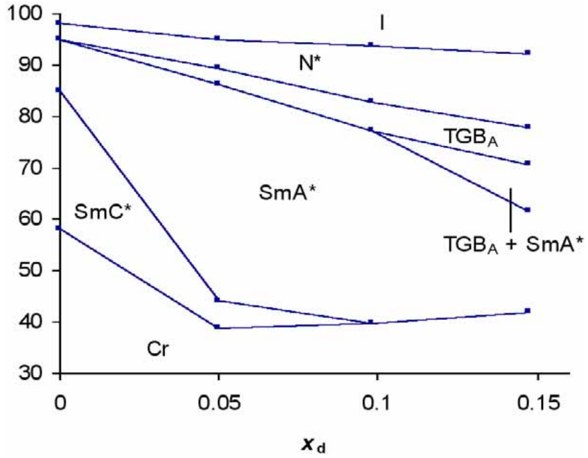
b) (*RS*)-**5a**, 0% ee



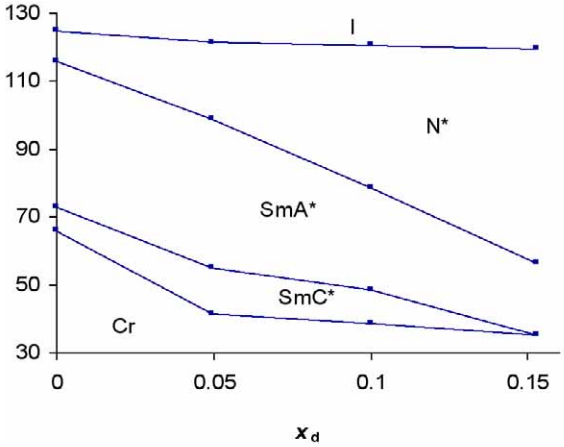
3. PHASE DIAGRAMS

a) Mixtures of (*R*)-**5b** in **PhP**, **NCB76**, **PhB** and **DFT**

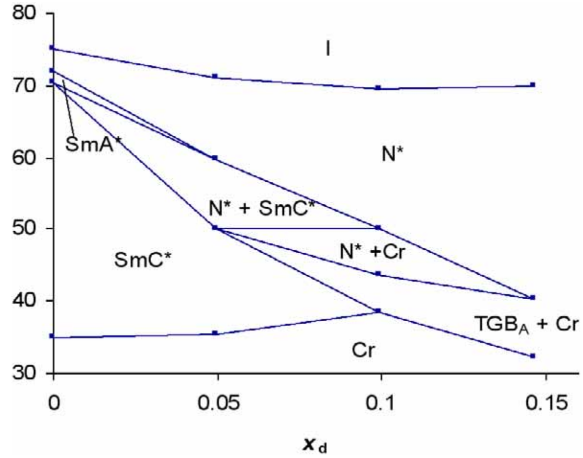
PhP



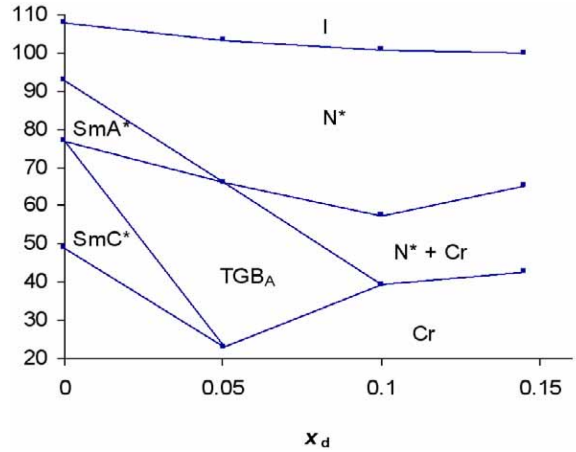
NCB76



PhB

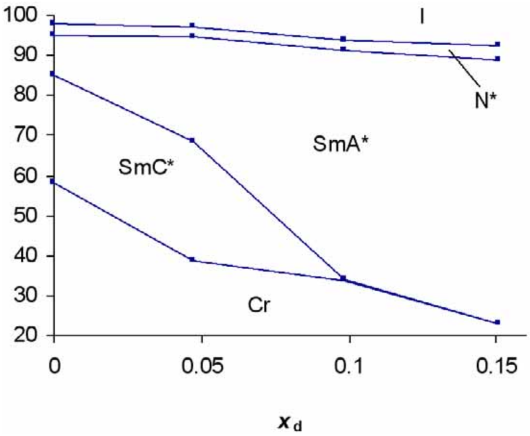


DFT

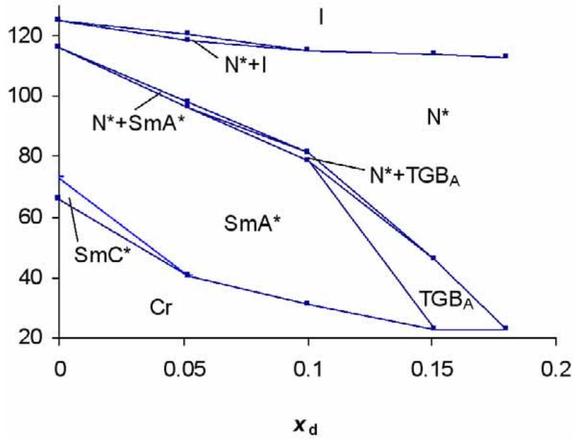


b) Mixtures of (*R*)-**5c** in **PhP**, **NCB76**, **PhB** and **DFT**

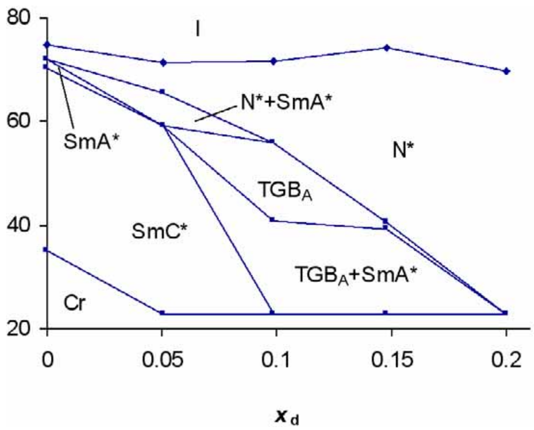
PhP



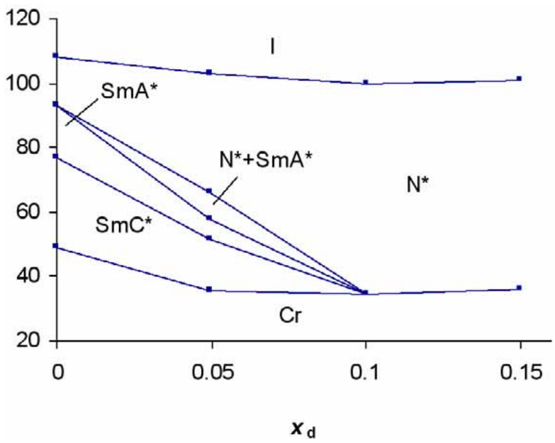
NCB76



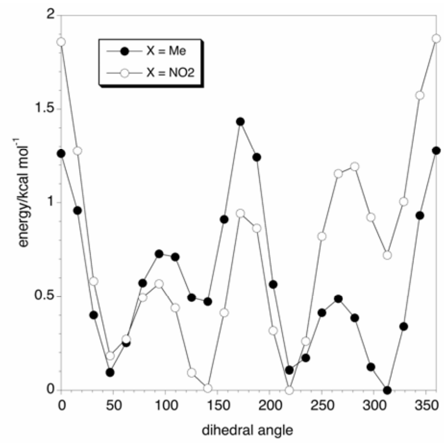
PhB

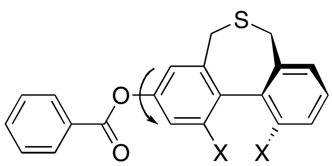


DFT



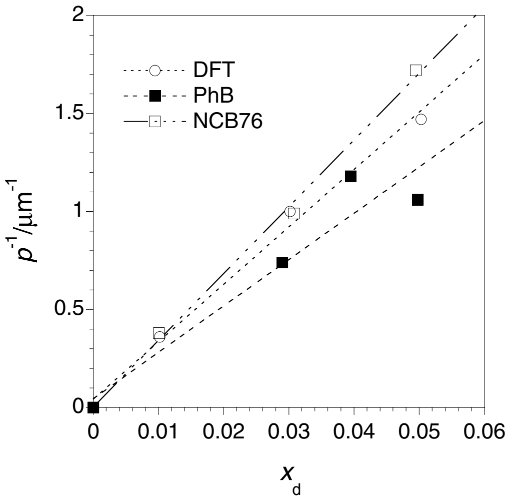
4. CONFORMATIONAL ANALYSIS (RHF/AM1)



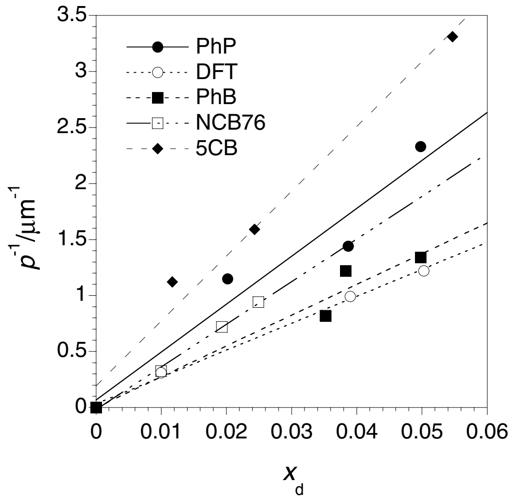


5. HELICAL TWISTING POWER MEASUREMENTS

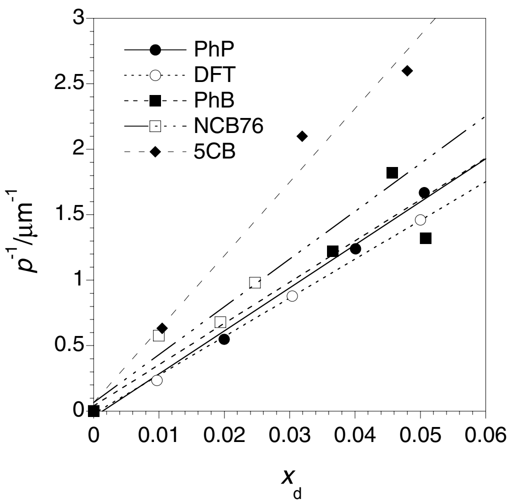
a) (*S*)-**5a** in **DFT**, **PhB** and **NCB76**



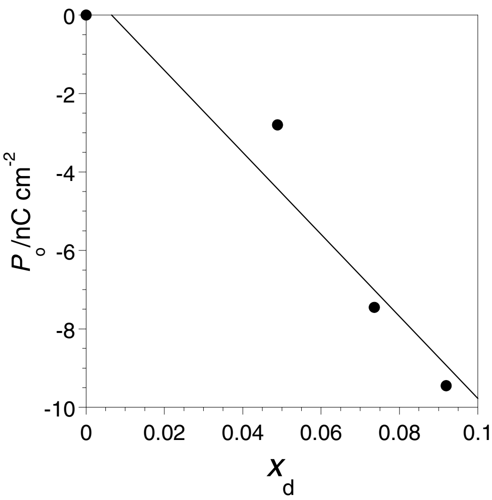
b) (*R*)-**5b** in **PhP**, **DFT**, **PhB** and **NCB76** and **5CB**



c) (*R*)-**5c** in **PhP**, **DFT**, **PhB** and **NCB76** and **5CB**



6. POLARIZATION POWER MEASUREMENTS: (*S*)-5a in PhP



REFERENCES

1. P. Keller, *Ferroelectrics*, 1984, **58**, 3.
2. G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *J. Chem. Soc., Perkin Trans. 2*, 1989, 2041.
3. P. J. Montoya-Pelaez, Y.-S. Uh, C. Lata, M. P. Thompson, R. P. Lemieux and C. M. Crudden, *J. Org. Chem.*, 2006, **71**, 5921.
4. A. J. Y. Lau, R. O. Heuckeroth and P. S. Mariano, *J. Am. Chem. Soc*, 1987, **109**, 2738.
5. V. E. Williams and R. P. Lemieux, *Chem. Commun.*, 1996, 2259.
6. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.*, 1983, **22**, L661.
7. D. M. Walba, in *Advances in the Synthesis and Reactivity of Solids*, ed. T. E. Mallouck, JAI Press, Ltd., Greenwich, CT, Editon edn., 1991, vol. 1, p. 173.