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Stabilization of the blue phases of simple rodlike monoester compounds by addition of their achiral homologues

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Expermental

A typical procedure for synthesis of esters (synthesis of 1). 4-(4-(*R*)-1-Methylheptyloxy-phenyl)benzoic acid (**8**) and 4-(4-(*R*)-1-methylheptyloxyphenyl)phenol (**9**) were obtained by Mitsunobu reaction of (*S*)-1-methylheptanol with 4-(4-hydroxyphenyl)-benzoic acid and 4,4'-biphenol, respectively. Reaction of **8** with thionyl chloride gave 4-(4-(*R*)-1- methylheptyloxyphenyl)benzoyl chloride (**10**).

Into a three-necked 100mL-round bottom flask were added **10** (145 mg, 0.420 mmol), **9** (133 mg, 0.446 mmol), 4-(dimethylamino)pyridine (5 mg, 0.04 mmol), dichloromethane (30 mL), and triethylamine (0.12 mL, 0.90 mmol). The solution was stirred for 24 h at room temperature. Distilled water (50 mL) was added and the solution was extracted with chloroform (100mL × 4). The solution was dried over anhydrous magnesium sulfate, filtrated with suction, and concentrated by a rotary evaporator. The crude mixture was separated by column chromatography on silica gel eluting with chloroform-hexane (1:5) to give a white solid (**1**).

4-(4-(*R*)-1-Methylheptyloxyphenyl)phenyl 4-(4-(*R*)-1-methyl-heptyloxyphenyl)benzoate (1). Yield: 41%; ν_{max}(KBr)/cm^{-1} 2929, 2856, 1733, 1496, 1466, 1376, 1079, 830, 723; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.82 (t, *J* = 6.7 Hz, 6H), 1.18-1.44 (m, 20H), 1.48-1.56 (m, 4H), 1.66-1.70 (m, 2H), 4.33 (sex, *J* = 6.0, 1H), 4.38 (sex, *J* = 6.0 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 4H), 7.62 (d, *J* = 8.5 Hz, 2H), 8.20 (d, *J* = 8.6 Hz, 2H); δ_C(99.45 MHz; $CDCl_3$; Me_4Si) 14.1, 19.8, 22.6, 25.6, 29.3, 31.8, 36.5, 74.0, 108.2, 116.1, 116.2, 121.6, 126.6, 127.5, 127.7, 128.2, 128.4, 130.7, 131.8, 132.7, 138.7, 146.0, 149.9, 157.9, 158.7; HRMS (FAB) 606.3698 (M^+. $C_{41}H_{50}O_4$ requires 606.3709); $[\alpha]_D^{27}$ -2.61 (c 0.114 in $CHCl_3$).

4-(4-(*R*)-1-Methylheptyloxyphenyl)phenyl 4-(4-octyloxy-phenyl)benzoate (2). Yield 30%; ν_{max}(KBr)/cm^{-1} 2923, 2853, 1729, 1496, 1474, 1376, 1074, 826, 720; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.88 (t, *J* = 6.7 Hz, 3H), 0.91 (t, *J* = 6.7 Hz, 3H), 1.30-1.48 (m, 18H), 1.55-1.62 (m, 4H), 1.73-1.86 (m, 3H), 4.02 (t, *J* = 6.5 Hz, 2H), 4.40 (sex, *J* = 6.0 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 8.25 (d, *J* = 8.6 Hz, 2H); δ_C(99.45 MHz; $CDCl_3$; Me_4Si) 14.1, 19.8, 22.6, 25.6, 29.2, 29.3, 29.4, 31.8, 68.2, 115.0, 116.1, 121.9, 126.6, 127.5, 127.7, 128.1, 128.3, 130.7, 132.0, 132.6, 138.7, 157.9; HRMS (FAB) 606.3659 (M^+. $C_{41}H_{50}O_4$ requires 606.3709); $[\alpha]_D^{27}$ -1.34 (c 0.149 in $CHCl_3$).

4-(4-Octyloxyphenyl)phenyl 4-(4-octyloxyphenyl)benzoate (3). Yield 38%; ν_{max}(KBr)/cm^{-1} 2921, 1733, 1498, 1474, 1396, 1085, 834, 721; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.85 (t, *J* = 7.1 Hz, 6H), 1.30-1.48 (m, 18H), 1.53-1.59 (m, 4H), 1.79-1.84 (m, 2H), 4.00 (t, *J* = 6.6 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 4H), 7.70 (d, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 8.2 Hz, 2H); δ_C(99.45 MHz; $CDCl_3$; Me_4Si) 14.1, 22.7, 26.0, 28.5, 29.3, 29.4, 31.8, 68.1, 105.2, 114.8, 115.0, 116.5, 121.9, 126.6, 127.7, 128.1, 128.4, 130.7, 132.0, 132.7, 149.9, 156.0, 158.8; HRMS (FAB) 606.3676 (M^+. $C_{41}H_{50}O_4$ requires 606.3709).

4-(4-(*R*)-1-Methylheptyloxyphenyl)phenyl 4-phenylbenzoate (4). Yield 55%; ν_{max}(KBr)/cm^{-1} 2928, 2856, 1742, 1604, 1496, 1288, 1272, 1227, 1082, 806, 741, 696; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.89 (t, *J* = 6.7 Hz, 3H), 1.29-1.47 (m, 10H), 1.56-1.61 (m, 2H), 1.74-1.77 (m, 1H), 4.39 (sex, *J* = 6.0 Hz, 1H), 6.96 (dd, *J* = 8.9, 1.2 Hz, 2H), 7.27 (dd, *J* = 8.9, 1.2 Hz, 2H), 7.39-7.51 (m, 5H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 8.28 (d, *J* = 8.3 Hz, 2H); δ_C(99.45 MHz; $CDCl_3$; Me_4Si) 14.1, 19.8, 22.6, 25.5, 29.3, 31.8, 36.5, 74.0, 116.1, 121.9, 127.2, 127.3, 127.7, 128.1, 128.2, 128.3, 129.0, 130.7, 132.6, 138.7, 139.8, 146.3, 149.8, 157.9, 165.2; HRMS (FAB) 478.2489 (M^+. $C_{33}H_{34}O_3$ requires 478.2508); $[\alpha]_D^{28.5}$ -2.25 (c 0.300 in $CHCl_3$).

Synthesis of 7. 4-(4-Octyloxyphenyl)benzyl chloride (**11**) was obtained by reaction of thionyl chloride and 4-(4-octyloxy-phenyl)benzyl alcohol which was prepared by alkylation of ethyl 4-(4-hydroxyphenyl)benzoate followed by reduction with $LiAlH_4$.
Into a three-necked 100mL-round bottom flask were added **9** (100 mg, 0.335 mmol), THF (30 mL), and sodium hydride (60% dispersion in paraffin liquid, 24 mg, 1.0 mmol), and the solution was stirred for 30 min. A solution of **11** (111 mg, 0.335 mmol) in THF (5mL) and tetrabutylammonium iodide (37 mg, 0.10 mmol) were added to the solution. The solution was stirred for 24 h at room temperature. Distilled water (50 mL) was added and the solution was extracted with chloroform (100mL × 4). The solution was dried over anhydrous magnesium sulfate, filtrated with suction, and concentrated by a rotary evaporator. The crude mixture was separated by column chromatography on silica gel eluting with chloroform-hexane (1:1) to give a white solid (**7**).

4-(4-(*R*)-1-Methylheptyloxyphenyl)phenyl 4-(4-octyloxy-phenyl)methyl ether (7). Yield 56%; ν_{max}(KBr)/cm^{-1} 2921, 2852, 1500, 1465, 1379, 1049, 808, 722; δ_H(400 MHz; $CDCl_3$; Me_4Si) 0.87 (t, J = 6.7 Hz, 3H), 0.90 (t, J = 6.7 Hz, 3H), 1.29-1.47 (m, 17H), 1.53-1.59 (m, 6H), 1.71-1.84 (m, 2H), 4.00 (t, J = 6.6 Hz, 2H), 4.37 (sex, J = 6.0 Hz, 1H), 5.12 (s, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 8.8 Hz, 2H), 7.44-7.53 (m, 8H), 7.58 (d, J = 8.7 Hz, 2H); δ_C(99.45 MHz; $CDCl_3$; Me_4Si) 14.1, 19.8, 22.7, 25.6, 26.1, 29.3, 29.4, 31.8, 36.5, 68.1, 73.3, 74.0, 114.8, 115.1, 116.1, 126.9, 127.7, 128.0, 128.1, 133.0, 133.8, 135.3, 157.4, 157.9; HRMS (FAB) 592.3911 (M^+. $C_{41}H_{52}O_3$ requires 592.3916); $[\alpha]_D^{27}$ +1.08 (c 0.369 in $CHCl_3$).

Polarized optical microphotographs

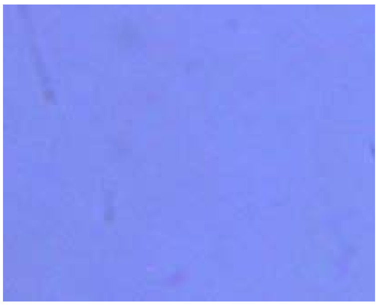


Figure 1S. Microphotograph of the blue phase of **1** on heating (600×, 151.0°C).

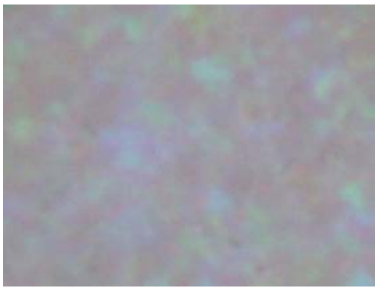


Figure 2S. Microphotograph of the blue phase of **2** on heating (600×, 240.8°C).

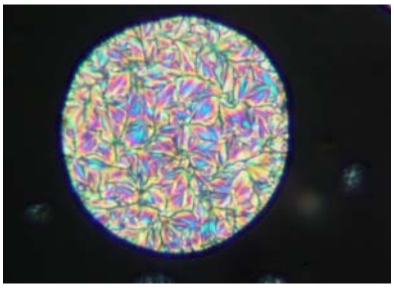


Figure 3S. Microphotograph of the chiral nematic phase of **2** on heating (600×, 239.0°C).

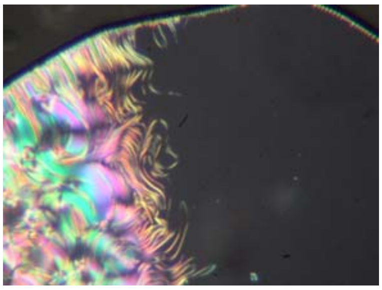


Figure 4S. Microphotograph of the transition from the SmA phase to the TGBA phase of **2** on heating (600×, 232.5°C).

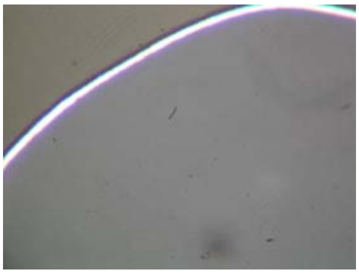


Figure 5S. Microphotograph of the SmA phase of **2** on heating (600×, 225°C).

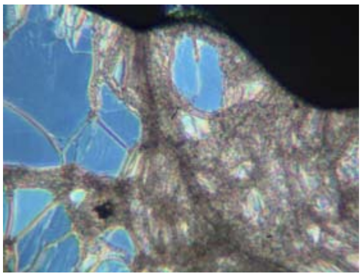


Figure 6S. Microphotograph of the SmC* phase of **2** on heating (600×, 180.0℃).

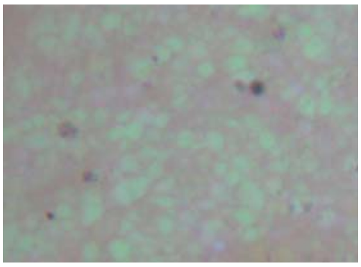


Figure 7S. Microphotograph of the blue phase of the mixture of **1** and **3** at the ratio of 1:1 on heating (600×, 229.0°C).

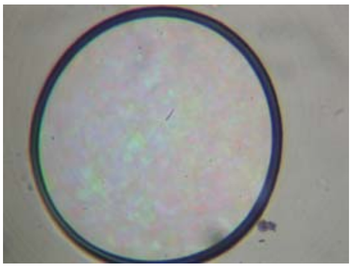


Figure 8S. Microphotograph of the blue phase of the mixture of **1** and **6** at the ratio of 1:1 on heating (600×, 125.0°C).

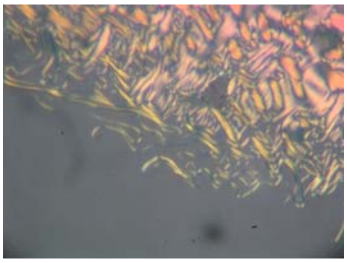


Figure 9S. Microphotograph of the TGBA phase of the mixture of **1** and **4** at the ratio of 1:1 on cooling (600×, 147.5°C).

Table S1. Phase transition temperatures of the mixtures of **1** and **3**.[a]

Mole fraction	*Cr*		*SmC*		*N*		*BP*		*Iso*
0.0	●	96.3	●	141.5	●	165.0	●	166.6	●
0.1	●	99.0	●	147.1	●	177.3	●	179.4	●
0.2	●	101.0	●	157.8	●	192.6	●	195.0	●
0.3	●	101.6	●	163.5	●	204.4	●	207.7	●
0.4	●	102.3	●	190.9	●	240.3	●	245.3	●
0.5	●	103.4	●	186.5	●	250.6	●	254.9	●
0.6	●	106.0	●	176.1	●	253.4	●	256.4	●
0.7	●	109.5	●	178.0	●	256.0	●	258.0	●
0.8	●	138.4	●	209.5	●		-	252.8	●
0.9	●	153.3	●	258.1	●		-	282.8	●
1.0	●	159.4	●	269.4	●		-	269.4	●

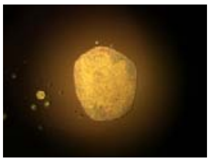
[a] The temperature ranges were measured by POM. The heating and cooling rates are 0.1°C/min.

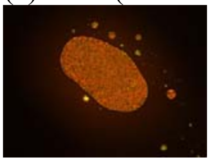
Table S2. Phase transition temperatures of the mixtures of **1** and **6**.[a]

Mole fraction	*Cr*		*SmC*		*N*		*BP*		*Iso*
0.0	●	96.3	●	141.5	●	166.1	●	167.7	●
0.1	●	88.5	●	131.0	●	156.5	●	157.7	●
0.2	●	71.1	●	125.1	●	151.0	●	152.1	●
0.3	●	52.3	●	121.9	●	148.4	●	149.5	●
0.4	●	42.8	●	120.3	●	146.2	●	147.3	●
0.5	●	37.0	●	97.6	●	132.6	●	133.6	●
0.6	●	24.4	●	93.6	●	118.7	●	119.6	●
0.7	●	36.7	●	86.5	●		-	109.0	●
0.8	●	29.5	●	85.8	●		-	109.3	●
0.9	●	28.8	●	79.8	●		-	100.1	●
1.0	●	63.3	●	76.4	●		-	94.4	●

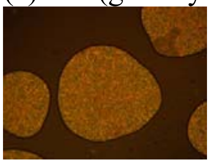
[a] The temperature ranges were measured by POM. The heating and cooling rates are 0.1°C/min.

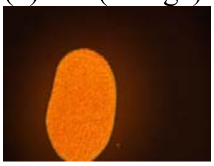
Selective refractions of the pure 1 (10:0) and the mixtures of 1 and 3 (9:1, 8:2, 7:3, 6:4, and 5:5). The selective refractions of the pure chiral compound **1** and the mixtures of **1** and achiral compound **3** were carried out by POM at $T_{bp\text{-}N}-T = 5$ (K) ($T_{bp\text{-}N}$: transition temperature of the BP and N) without the polarizers.


(a) 10:0 (no color)


(b) 9:1 (orange-red)


(c) 8:2 (green-yellow)


(d) 7:3 (orange)


(e) 6:4 (orange-red)


(f) 5:5 (red-no color)

Figure 10S. Selective reflections of the mixtures **1**:**3** against the molar ratios. Pure chiral compound **1** did not have color (a). The mixtures at 9:1 and 8:2 showed orange-red (b) and green-yellow (c), which indicated that the helical pitch became shorter by addition of achiral compound **3**. However, the mixtures at 7:3 and 6:4 showed orange (d) and orange-red (c), and at 5:5 it exhibited pale red, which meant that the helical pitch become longer by addition of the achiral dopant.