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Synthesis and Mesomorphic Properties of Ferroelectric Liquid Crystals Bearing Trans 4-Alkoxycyclohexylpyrimidines

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A homologous series of chiral trans-4-alkoxycyclohexylpyrimidines were synthesized and their mesomorphic properties were evaluated with a DSC and a polarizing microscope. It was found that the presence of a trans-1, 4-disubstituted cyclohexane ring strongly promoted the formation of the SB phase and seems to suppress the formation of the chiral smectic C (SC*) phase.

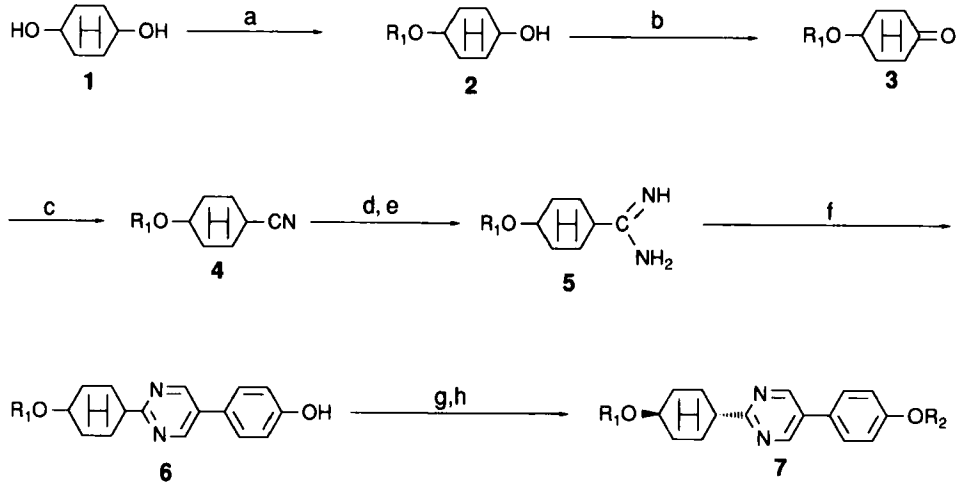
Keywords: ferroelectric liquid crystal, phase transition, cyclohexylpyrimidine

INTRODUCTION

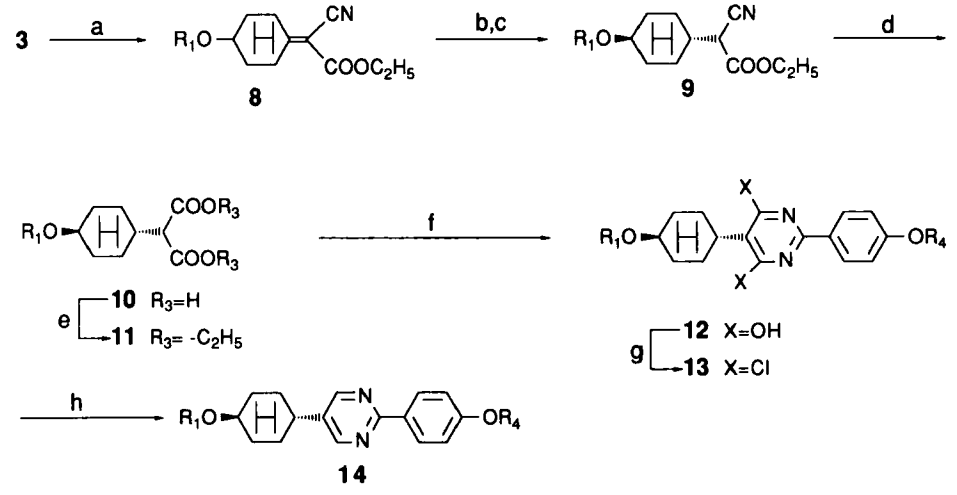
Since the discovery of ferroelectricity in the chiral smectic C (SC*) phase by R. Meyer in 1975[1] and the proposal of electro-optical devices using ferroelectric liquid crystals by Clark and Lagerwall in 1980,[2] extensive studies have been done on ferroelectric liquid crystal materials and their applications. As pointed out by Goodby, ferroelectric liquid crystals require at least two aromatic rings in the core and two terminal chains at the end of the core, one of which contains at least one chiral group.[3] The effects of introducing an additional trans-1, 4-disubstituted cyclohexane ring into various phenyl benzoates exhibiting a chiral smectic C phase have been reported and the significant improvements in the liquid crystal transition temperature were observed.[4] Moreover, the use of the cyclohexane ring as a structural element in liquid crystals is well known to show lower viscosity than that of the analogous phenyl ring compound.[5] So, we try to enhance the thermodynamic stabilities of the liquid crystals having 2 or 5-phenylpyrimidine as a core by introducing a trans-1, 4-disubstituted cyclohexane ring without increasing viscosity.

SYNTHESIS

The compounds studied were prepared as outlined in Scheme I and Scheme II. 1,4-Cyclohexanediol (mixture of cis and trans) was alkylated with alkyl bromide in the presence of sodium hydride followed by oxidation with Jone's reagent to yield 4-alkoxycyclohexanone (**3**). A reaction of **3** with *p*-toluenesolfonylmethyl isocyanide gave 4-alkoxycyclohexylcyanide (**4**). **4** was treated with HCl/EtOH,



SCHEME I (a) R_1Br, NaH, DMF, 100°C, 8 h; (b) CrO_3, H_2SO_4, acetone, 25°C, 8 h; (c) *p*-toluenesulfonylmethyl isocyanide, t-BuOK, THF, 25°C, 8 h; (d) HCl, EtOH, 25°C, 8 h; (e) NH_3, EtOH, 25°C, 8 h; (f) 2-(4-hydroxyphenyl)-3-dimethylaminoacrolein, pyridine, 100°C, 8 h; (g) R_2OTs, NaH, DMF, 25°C, 8 h; (h) separation.



SCHEME II (a) $NCCH_2COOC_2H_5$, $AcONH_4$, benzene, reflux, 66 h; (b) $NaBH_4$, EtOH, 25°C, 1 h; (c) separation; (d) KOH, EtOH-H_2O, reflux, 64 h; (e) H_2SO_4, EtOH, reflux, 20 h; (f) 4-alkoxybenzamidine-HCl, $NaOCH_3$, MeOH, reflux, 16 h; (g) $POCl_3$, N,N-diethylaniline, reflux, 16 h; (h) H_2/Pd-C, MgO, EtOH-THF-H_2O, 25°C, 6 h.

subsequent NH_3/EtOH to afford 4-alkoxy cyclohexanecarboxamidine (**5**). Condensation of **5** with 2-(4-hydroxyphenyl)-3-dimethylaminoacrolein afforded a 2-cyclohexyl-5-phenylpyrimidine derivative (**6**), which was alkylated with tosylate of appropriate alcohol to give a cis-trans mixture of 2-(4-alkoxycyclohexyl)-5-(4-alkoxyphenyl)pyrimidine (**7**). The trans isomers were separated easily by silica-gel column chromatography. Synthesis of compound **14** was carried out as follows: **3** was condensed with ethyl cyanoacetate yielding the cyclohexylidene derivative (**8**), which was reduced with sodium borohydride to give a cis-trans isomers of cyano acetate derivatives (**9**). The cis-trans isomers could be separated easily by silica-gel column chromatography in this stage. Hydrolysis of **9** followed by esterification in the conventional manner provided **11**. Construction of the pyrimidine ring was achieved by condensation of **11** with 4-alkoxybenzamidine. Chlorination of **12** followed by catalytic hydrogenation with palladium-carbon afforded **14**. Final products were purified by column chromatography on silica-gel using hexane and ether as the eluent followed by recrystallization from ethanol.

The ^{1}H NMR spectrum data for compound **7b** showed the C-4 proton signals for the cyclohexane ring of the *trans* and *cis* isomers at $\delta = 3.36$ and $\delta = 3.57$, respectively. Therefore, the purity of trans isomers can be checked by the disappearance of the cis isomer's peak. The purities of the trans isomer of the other compounds were checked in the same manner.

RESULTS AND DISCUSSION

The transition temperatures of the homologous series **7** and **14** are given in Tables I and II. The plots of the transition temperatures against the number of carbon atoms (m, n) of the homologous series **7** and **14** are shown in Figures 1 and 2, respectively.

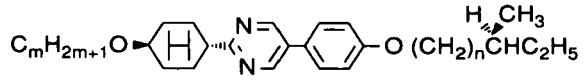
The homologous series of **7** exhibited I-SA-SB-Cr mesomorphogy and the chiral smectic C (SC*) phase could not be observed in any member. The homologous series of **14** also tends to show I-SA-SB-Cr phase sequences. Chiral smectic C (SC*) behavior is observed only in the case of homologs **14f** and **14g** with long terminal alkyl chains.

From a comparison of the mesomorphic behavior of these two homologous series, it is clear that the thermal stabilities of the mesophases of the homologous series of **14** is higher than that of the homologous series of **7** and the temperature range of mesophases of the homologous series of **14** is wider than that of the homologous series of **7**. This result suggests that the 2-phenylpyrimidine skeleton of the homologous series of **14** contributes to the stability of the mesophases, that is, the planer structure of the 2-phenylpyrimidine skeleton should lead to an increased polarizability of the central core, because of more extended conjugation, and thus to an enhanced smectic thermal stability.[6] Moreover, the homologous series of **7** shows a stronger tendency to generate the SB phase than that of the homologous series of **14**.

Both homologous series **7** and **14** have strong tendencies to show I-SA-SB-Cr phase sequences, though analogous 2-phenylpyrimidine[7] and 5-phenylpyrimidine[8]

TABLE I

Phase transition temperatures of homologous series 7[a]



Compound	m	n	Cr	SB	SA	Iso
7a	8	1	· 46.0	· 108.0	· 125.0	·
7b	8	3	· 47.0	· 102.0	· 127.0	·
7c	8	5	· 42.0	· 107.0	· 161.6	·
7d	9	1	· 39.0	· 101.0	· 116.0	·
7e	9	3	· 37.0	· 100.0	· 119.0	·
7f	9	5	· 37.0	· 103.0	· 112.0	·
7g	10	1	· 42.0	· 102.0	· 110.0	·
7h	10	3	· 44.0	· 101.0	· 121.0	·
7i	10	5	· 33.0	· 109.0	· 124.0	·

a) Phase transition temperatures were obtained at a heating or cooling rate of 5℃/min. Cr; crystalline solid, SB; smectic B phase, SA; smectic A phase, Iso; isotropic liquid phase.

derivatives show I-SA-SC-Cr phase sequences. Obviously, the presence of an additional 1,4-disubstituted cyclohexane ring strongly promotes the occurrence of a smectic B phase and seems to suppress the appearance of a chiral smectic C phase. Similar results were obtained by S. M. Kelly[9] for the derivatives of trans 4-alkylcyclohexane-1-carboxylates of 4-{5-((S)-6-methyloctyl)-2-pyrimidinyl}phenol.

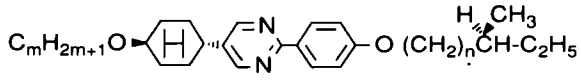
EXPERIMENTAL

IR, ^{1}H NMR and mass spectra were recorded on a Shimadzu IR-408, Varian EM-360 and Hitachi M-80, respectively, under standard conditions. Final products were purified by column chromatography on silica-gel followed by recrystallization from ethanol. The phase transition temperatures were determined by using a Rigaku Denki DSC-8230 apparatus at a constant heating/cooling rate of 5°C/min. Identity of the mesophases was confirmed by examining the texture of a thin sample sandwiched between glass slides using a Nikon XTP-II polarizing microscope in conjunction with a Mettler FP-82 hot stage and FP-80 control unit.[10] The preparations of compounds **7b** and **14a** as representatives are given below.

4-n-Octyloxycyclohexanol (**2**, R_1 = *n-octyl*). To a suspension of sodium hydride (60% assay in mineral oil, 20.0 g, 0.50 mol) in dry DMF (500 ml) was added dropwise 1,4-cyclohexanediol (58.1 g, 0.50 mol). After stirring at 80°C for 6 h, *n*-

TABLE II

Phase transition temperatures of homologous series **14**[a]



Compound	m	n	Cr	SB	Sc*	SA	Iso
14a	8	1	· 64.6	· 104.9	—	· 160.5	·
14b	8	3	· 68.0	· 101.0	—	· 160.9	·
14c	8	5	· 77.2	· 109.3	—	· 161.6	·
14d	9	1	· 61.7	· 108.2	—	· 156.0	·
14e	9	3	· 63.5	· 103.0	—	· 157.4	·
14f	9	5	· 69.0	· 110.8	· 120.4	· 158.7	·
14g	12	3	· 50.5	· 114.3	· 122.9	· 149.8	·

a) Phase transition temperatures were obtained at a heating or cooling rate of 5℃/min. Cr; crystalline solid, SB; smectic B phase, Sc*; chiral smectic C phase, SA; smectic A phase, Iso; isotropic liquid phase.

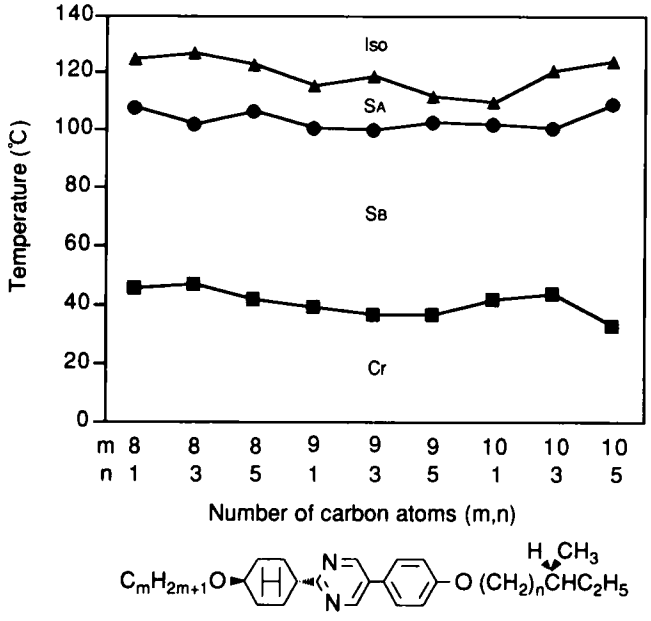


FIGURE 1 Plots of transition temperatures against the number of carbon atoms (m, n) of homologous series **7**.

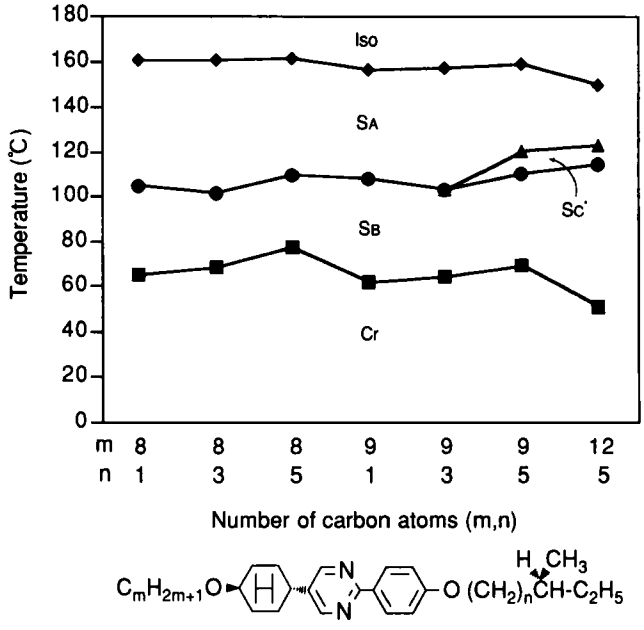


FIGURE 2 Plots of transition temperatures against the number of carbon atoms (m, n) of homologous series **14**.

octylbromide (96.6 g, 0.50 mol) was added, and then heated at 90°C for 15 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was extracted several times with ether. The extracts were washed with water and evaporated in vacuo to leave an oil, which was purified by distillation under reduced pressure to afford 4-*n*-octyloxycyclohexanol (**2**, R_1 = *n*-octyl) (38.7 g, 33.9%) as an oil. Bp 125–130°C (4 mmHg); IR (film) 3330, 1450, 1360, 1335, 1280, 1250, 1228, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.72–1.00 (3H, m), 1.03–2.10 (20H, m), 3.13–3.87 (4H, m); Mass: m/z 228 (m^+).

*4-n-Octyloxycyclohexanone (**3**, R_1 = n-octyl).* To an ice-cooled solution of 4-*n*-octyloxycyclohexanol (**2**, R_1 = *n*-octyl, 8.67 g, 38.0 mmol) in acetone (260 ml) was added a freshly prepared solution of CrO_3 (4.18 g, 41.8 mmol) and conc.H_2SO_4 (3.80 ml, 77.5 mmol) in water (13.0 ml) over 30 min. After stirring for 1 h at room temperature, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting residue was extracted several times with ether and the extracts were washed with water, and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by column chromatography on a silica-gel with hexane-ether as eluent to yield 4-*n*-octyloxycyclohexanone (**3**, R_1 = *n*-octyl, 6.91 g, 80.4%) as an oil. IR (film) 1715, 1455, 1340, 1300 cm^{-1}; NMR ($CDCl_3$) δ = 0.89 (3H, m), 1.10–2.80 (20H, m), 3.50 (2H, t, *J* = 6Hz), 3.70 (1H, m); Mass: m/z 226 (m^+).

*4-n-Octyloxycyclohexyl cyanide (**4**, R_1 = n-octyl).* To a stirred solution of potassium t-butoxide (4.13 g, 36.8 mmol) in THF (90 ml) was added *p*-toluenesulfo-

nylmethyl isocyanide (7.19 g, 36.8 mmol) and 4-*n*-octyloxycyclohexanone (**3**, R_1 = *n*-octyl, 8.33 g, 36.8 mmol) at −10°C and the mixture was stirred at 0°C for 1 h. The reaction mixture was evaporated and the residue was extracted with ether. The extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was dissolved in methanol (20 ml). To this solution was added a solution of sodium (1.69 g) in methanol (60 ml), and then the mixture was refluxed for 1 h. The reaction mixture was evaporated and the residue was purified by column chromatography on a silica-gel with hexane-ether as eluent to yield 4-*n*-octyloxycyclohexyl cyanide (**4**, R_1 = *n*-octyl, 4.61 g, 52.7%) as an oil. IR (film) 2230, 1450, 1365, 1330 cm^{-1}; NMR ($CDCl_3$) δ = 0.73–1.00 (3H, m), 1.10–2.20 (21H, m), 2.40–2.73 (1H, m), 3.35 (2H, t, *J* = 7 Hz).

4-n-Octyloxycyclohexanecarboxamidine (**5**, R_1 = *n-octyl*). A mixture of 4-*n*-octyloxycyclohexyl cyanide (**4**, R_1 = *n*-octyl, 4.92 g, 20.7 mmol), ethanol (1.08 g) and hydrogen chloride (0.81 g) was stirred at room temperature for 66 h. The reaction mixture was evaporated and the residue was dissolved in ethanol (30 ml). To this solution was added a solution of ammonia (1.5 g, 88.2 mmol) in ethanol (15 ml) and the mixture was stirred at room temperature for 2 h. The reaction mixture was evaporated and the residue was diluted with 4 N NaOH and extracted twice with chloroform. The extracts were washed with water and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield 4-*n*-octyloxycyclohexanecarboxamidine (**5**, R_1 = *n*-octyl, 4.29 g, 81.4%). IR (film) 3400, 3300, 3140, 1635, 1590, 1150, 1105 cm^{-1}; NMR ($CDCl_3$) δ = 0.73–1.00 (3H, m), 1.10–2.20 (21H, m), 2.40–2.73 (1H, m), 3.35 (2H, t, *J* = 7 Hz).

5-(4-Hydroxyphenyl)-2-(4-n-octyloxycyclohexyl)pyrimidine (**6**, R_1 = *n-octyl*). A mixture of 4-*n*-octyloxycyclohexanecarboxamidine (**5**, R_1 = *n*-octyl, 3.21 g, 12.6 mmol) and 2-(4-hydroxyphenyl)-3-dimethylaminoacrolein (2.41 g, 12.6 mmol) in pyridine (40 ml) was stirred at 80°C for 18h. The reaction mixture was evaporated and the residue was extracted several times with ether. The extracts were washed with 5% HCl and water, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on a silica-gel with hexane-ether as eluent to yield 2-(4-*n*-octyloxycyclohexyl)-5-(4-hydroxyphenyl)pyrimidine (**6**, R_1 = *n*-octyl, 2.79 g, 59.7%) as crystal. IR (Nujol) 1600, 1580, 1535, 1510 cm^{-1}; NMR ($CDCl_3$) δ = 0.87 (3H, m), 1.10–2.40 (20H, m), 2.96 (1H, m), 3.24–3.70 (3H, m), 6.98 (2H, d, *J* = 9 Hz), 7.46 (2H, d, *J* = 9 Hz), 7.80 (1H, s), 8.87 (2H, s); Mass: m/z 382 (m^+).

(S)-5-{4-(4-Methylhexyloxy)phenyl}-2-(trans-4-octyloxycyclohexyl)pyrimidine (**7b**). To a suspension of sodium hydride (60% assay in mineral oil, 0.12 g, 2.61 mol) in dry DMF (10 ml) was added dropwise a solution of 2-(4-*n*-octyloxycyclohexyl)5-(4-hydroxyphenyl)pyrimidine (**6**, R_1 = *n*-octyl, 1.0 g, 2.61 mol) in dry DMF (5 ml). After stirring for half an hour, (*S*)-4-methylhexyl *p*-toluenesulfonate (0.85 g, 3.15 mol) was added and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into water and extracted several times with ether. The extracts were washed with water and dried over anhydrous $MgSO_4$.

The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography with hexane-ether as eluent followed by recrystallization from ethanol to yield (*S*)-5-{4-(4-methylhexyloxy)phenyl}-2-(trans-4-octyloxycyclohexyl)pyrimidine (**7b**, 0.68 g, 54.2%) as a colorless crystal. IR (Nujol) 1600, 1580, 1530, 1510, 1270, 1240, 1175, 1100, cm^{-1}; NMR ($CDCl_3$) δ = 0.70–2.35 (36H, m), 2.94 (1H, m), 3.36 (1H, m), 3.50 (2H, t, J = 7 Hz), 4.00 (2H, t, J = 6 Hz), 7.02 (2H, d, J = 9 Hz), 7.50 (2H, d, J = 9 Hz), 8.85 (2H, s); Mass: m/z 480 (m^+); Found: C, 77.66; H, 10.33; N, 5.80%. Calcd for $C_{31}H_{48}N_2O_2$: C, 77.45; H, 10.07; N, 5.83%.

Ethyl 4-n-octyloxycyclohexylidenecyanoacetate (**8**, R_1 = *n-octyl*). To a stirred solution of 4-*n*-octyloxycyclohexanone (**3**, R_1 = *n*-octyl, 4.53 g, 20.0 mmol) in benzene (50 ml) was added dropwise ethyl cyano acetate (4.52 g, 40.0 mmol) and ammonium acetate (0.31 g, 40.2 mmol), and then the mixture was refluxed azeotropically for 66 h. The reaction mixture was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography with hexane-ether as eluent to yield ethyl 4-*n*-octyloxycyclohexylidenecyanoacetate (**8**, R_1 = *n*-octyl, 6.28 g, 97.7%) as an oil. IR (film) 2210, 1725, 1600, 1450, 1385, 1360, 1330, 1275, 1258, 1225, 1200 cm^{-1}; NMR ($CDCl_3$) δ = 0.86 (17H, m), 1.10–2.00 (19H, m), 2.44–3.69 (7H, m), 4.24 (2H, q, J = 7 Hz); Mass: m/z 321 (m^+).

Ethyl 2-cyano-2-(trans-4-n-octyloxycyclohexyl)acetate (**9**). To an ice-cooled solution of ethyl 4-*n*-octyloxycyclohexylidenecyanoacetate (**8**, R_1 = *n*-octyl, 6.16 g, 19.2 mmol) in ethanol (15 ml) was added dropwise a solution of $NaBH_4$ (0.73 g, 19.3 mmol) in ethanol (15 ml). After stirring for 1 h at room temperature, the reaction mixture was concentrated under reduced pressure and the resulting residue was extracted several times with ether. The combined ethereal layers were washed with water, and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by silica-gel column chromatography with hexane-ether as eluent to yield ethyl 2-cyano-2-trans-4-*n*-octyloxycyclohexyl acetate (**9**, R_1 = *n*-octyl, 1.3 g, 20.9%) as an oil. IR (film) 2240, 1740, 1460, 1450, 1365, 1285, 1245, 1180, 1100 cm^{-1}; NMR ($CDCl_3$) δ = 0.80–1.04 (3H, m), 1.12—2.30 (24H, m), 3.14–3.23 (1H, m), 3.41 (1H, d, J, 6 Hz), 3.44 (2H, t, J = 7 Hz), 4.27 (2H, t, J = 7 Hz); Mass: m/z 323 (m^+).

2-(trans-4-n-Octyloxycyclohexyl) malonic acid (**10**, R_1 = *n-octyl*). To a stirred solution of ethyl 2-cyano-2-trans-4-*n*-octyloxycyclohexyl acetate (**9**, R_1 = *n*-octyl, 1.20 g, 3.71 mmol) in ethanol (4 ml) was added dropwise a solution of KOH (0.83 g, 14.8 mmol) in water (2 ml) and the mixture was refluxed for 64 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the resulting residue was added to water and acidified with aqueous HCl and extracted several times eith ether. The extracts were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was washed with *n*-hexane to yield 2-(trans-4-*n*-octyloxycyclohexyl)malonic acid (**10**, R_1 = *n*-octyl, 1.10 g, 94.8%). IR (Nujol) 2800, 1740, 1710, 1400, 1285, 1260, 1230, 1210,

1190, 1150 cm^{-1}; NMR ($CDCl_3$) δ = 0.81 (3H, m), 1.05–2.35 (21H, m), 3.08–3.62 (4H, m); Mass: m/z 314 (m^+).

Diethyl 2-(trans-n-octyloxycyclohexyl)malonate (**11**, R_1 = *octyl*). A solution of 2-(trans-4-*n*-octyloxycyclohexyl)malonic acid (**10**, R_1 = *n*-octyl, 1.02 g, 3.24 mmol) and conc. H_2SO_4 (0.016 ml, 0.30 mmol) in ethanol (20 ml) was heated under reflux for 20 h. The reaction mixture was evaporated under reduced pressure and the residue was extracted several times with ether. The extracts were washed successively with aqueous $NaHCO_3$ and water, and then dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by silica-gel column chromatography with hexane-ether as eluent to yield diethyl 2-(trans-*n*-octyloxycyclohexyl)malonate (**11**, R_1 = *n*-octyl, 1.14 g, 95.0%) as an oil. IR (film) 1750, 1730, 1460, 1450, 1360, 1310, 1280, 1230, 1170, 1100 cm^{-1}; NMR ($CDCl_3$) δ = 0.89 (3H, m), 1.08–2.27 (27H, m), 2.98–3.30 (1H, m), 3.15 (1H, d, *J* = 7 Hz), 3.43 (2H, t, *J* = 7 Hz), 4.22 (4H, q, *J* = 7 Hz); Mass: m/z 370 (m^+).

(S)-4,6-Dihydroxy-2-{4-(2-methylbutyloxy)phenyl}-5-(trans-4-octyloxycyclohexyl)pyrimidine (**12**, R_1 = *n-octyl*, R_2 = *(S)-2-methylbutyl*). A mixture of sodium (0.21 g, 9.1 mmol), diethyl 2-(trans-*n*-octyloxycyclohexyl)malonate (**11**, R_1 = octyl, 0.99 g, 2.67 mmol), and (*S*)-4-(2-methylbutoxy)benzamidine HCl (0.70 g, 2.67 mmol) in methanol (10 ml) was refluxed for 16 h. After cooling to room temperature, concentrated HCl (1.5 ml) was added and the resulting precipitate was collected by filtration, washed with water and dried at 60°C under reduced pressure for 8 h to yield (*S*)-4,6-dihydroxy-2-{4-(2-methylbutyloxy)phenyl}-5-(trans-4-octyloxycyclohexyl)pyrimidine (**12**, R_1 = *n*-octyl, R_2 = (*S*)-2-methylbutyl, 1.20 g, 83.3%): IR (Nujol) 2650, 1645, 1605, 1570, 1500, 1420, 1330, 1300, 1270, 1185, 1100 cm^{-1}; NMR ($CDCl_3$) δ = 0.80–1.20 (9H, m), 1.23–2.58 (24H, m), 2.80–3.35 (1H, m), 3.60–4.30 (5H, m), 7.27 (2H, d, *J* = 8 Hz), 8.04 (2H, d, *J* = 8 Hz); Mass: m/z 484 (m^+).

(S)-4,6-Dichloro-2-{4-(2-methylbutoxy)phenyl}-5-(trans-4-octyloxycyclohexyl)pyrimidine (**13**, R_1 = *n-octyl*, R_2 = *(S)-2-methylbutyl*). A mixture of (*S*)-4,6-dihydroxy-2-{4-(2-methylbutyloxy)phenyl}-5-(trans-4-octyloxy cyclohexyl)pyrimidine (**12**, R_1 = *n*-octyl, R_2 = (*S*)-2-methylbutyl, 2.17 g, 4.48 mmol), $POCl_3$ (10 ml, 107.3 mmol) and N,N-diethylaniline (1 ml, 6.70 mmol) was refluxed for 16 h. The reaction mixture was concentrated and the residue was extracted several times with ether. The combined organic layers were washed successively with water, 5% HCl, water, 5% $NaHCO_3$ and water, and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography using hexane-ether as eluent to yield (*S*)-4,6-dichloro-2-{4-(2-methylbutoxy)phenyl}-5-(trans-4-octyloxycyclohexyl)pyrimidine (**13**, R_1 = *n*-octyl, R_2 = (*S*)-2-methylbutyl, 1.70 g, 75.8%) as an oil. IR (film) 1600, 1575, 1540, 1510, 1480, 1445, 1400, 1300, 1265, 1245, 1160, 1100 cm^{-1}; NMR ($CDCl_3$) δ = 0.70–1.10 (9H, m), 1.12–2.60 (24H, m), 3.10–3.60 (4H, m), 3.60–4.12 (2H, m), 6.96 (2H, d, *J* = 8 Hz), 8.37 (2H, d, *J* = 8 Hz); Mass: m/z 520 (m^+).

(S)-2-{4-(2-Methylbutoxy)phenyl}-5-(trans-4-octyloxycyclohexyl)pyrimidine (**14a**). A mixture of (*S*)-4,6-dichloro-2-{4-(2-methylbutoxy)phenyl}-5-(trans-4-octyloxy cyclohexyl)pyrimidine (**13**, R_1 = *n*-octyl, R_2 = (*S*)-2-methylbutyl, 1.61 g, 3.10 mmol), MgO (0.5 g) and 10% palladium-carbon (0.30 g) in ethanol (15 ml), THF (15 ml) and water (2 ml) was stirred under hydrogen atmosphere. After the reaction was complete, the catalyst was filtered off and the filtrate was evaporated. The residue was diluted with water and extracted several times with ether. The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography using hexane-ether as eluent followed by recrystallization from ethanol to yield **14a** (0.68 g, 48.9%). IR (Nujol) 1603, 1580, 1535, 1510, 1430, 1330, 1310, 1285, 1245, 1160, 1100 cm^{-1}; NMR ($CDCl_3$) δ = 0.86–1.12 (9H, m), 1.13–2.37 (15H, m), 2.57 (1H, m), 3.50 (1H, m), 3.64 (2H, t, J = 7 Hz), 3.92 (2H, m), 7.03 (2H, d, J = 9 Hz), 8.43 (2H, d, J = 9 Hz), 8.67 (2H, s); Mass: m/z 452 (m^+); Found: C, 76.60; H, 10.04; N, 6.13%. Calcd. for $C_{29}H_{44}N_2O_2$: C, 76.94; H, 9.79; N, 6.18%.

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