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Synthesis and Mesomorphic Properties of Ferroelectric Liquid Crystals Bearing 5-Phenylpyrimidine Rings

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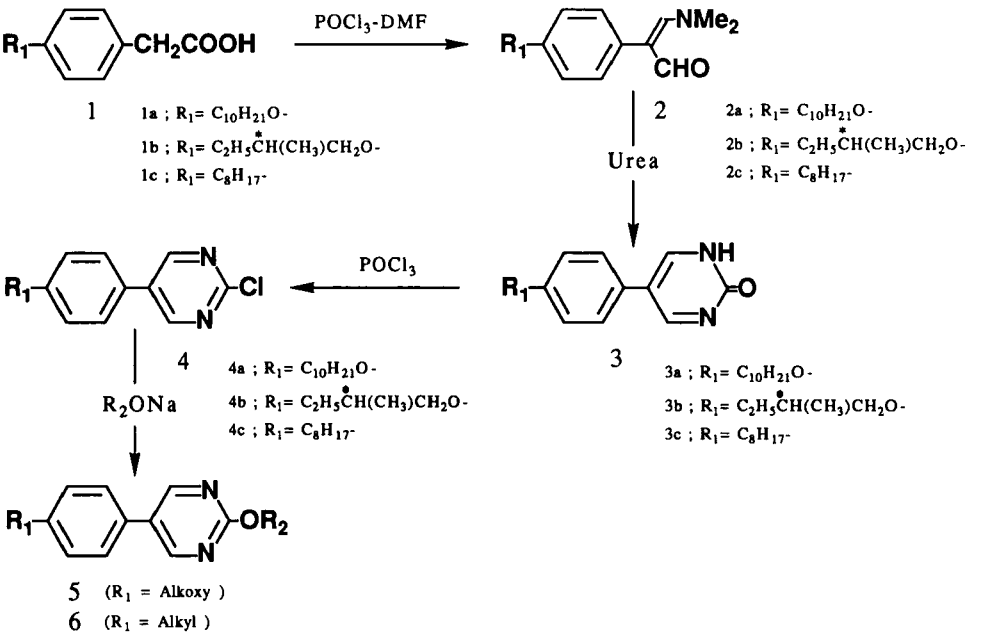
Seventeen homologs of chiral 5-phenylpyrimidines were synthesized and their mesomorphic properties were evaluated with a DSC and a polarizing microscope. All compounds studied possessed an alkyl or alkoxyl side chain at the *p*, *p'* position of the 5-phenylpyrimidine core and an optically active carbon atom at one of the terminal chains. Most of the series exhibited mesomorphic properties and five of them showed a chiral smectic C phase. We also measured some compounds for spontaneous polarizations (Ps) and optical response times (τ), and found that the magnitudes of the spontaneous polarizations (Ps) were very small and the optical response times (τ) were very fast.

INTRODUCTION

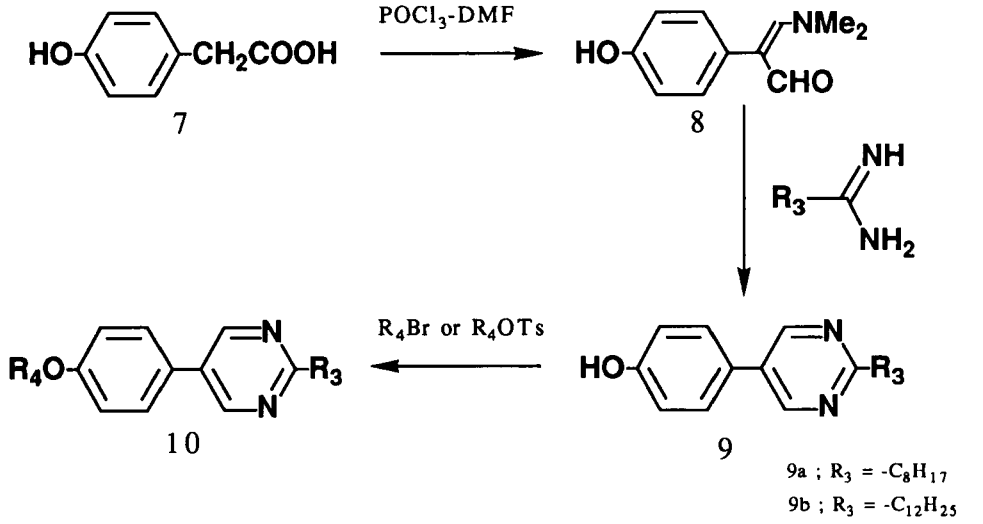
Since the discovery of ferroelectricity in the chiral smectic C phase of DOBAMBC (*p*-dodecylbenzylidene-*p'*-amino-2-methylbutylcinnamate) by Meyer,[1] extensive studies have been done on ferroelectric liquid crystal materials and their applications. As pointed out by Goodby,[2] ferroelectric liquid 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. To study the relationship between the molecular structure and the mesomorphic properties of liquid crystals, we synthesized chiral compounds which have heterocycles in the core and investigated their mesomorphic properties. In this paper, we describe the synthesis and the mesomorphic properties of several new chiral compounds bearing 5-phenylpyrimidine rings.

SYNTHESIS

The compounds studied were prepared as outlined in Scheme I and Scheme II. As shown in Scheme I, the Vilsmeier reaction of 4-substituted phenylacetic acid (**1a–1c**) and subsequent alkaline hydrolysis afforded 2-(4-substituted phenyl)-3-dimethylamino acroleine (**2a–2c**) in 40–80% yield. The starting materials, 4-decyl-



SCHEME I Synthesis route of the compounds **5** and **6**.



SCHEME II Synthesis route of the compound **10**.

oxyphenylacetic acid (**1a**) and (s)-4-(2-methylbutyloxy)phenylacetic acid (**1b**), were obtained by etherification of commercially available 4-hydroxyphenylacetic acid with decylbromide or (s)-2-methylbutyloxy-*p*-toluenesulfonate, respectively. To obtain 4-octylphenylacetic acid (**1c**) we used the method reported by Tamura[3] in which the Fridel-Crafts reaction of alkylbenzene with ethyl 1-chloro-1-(methylthio)acetate followed by desulfurization with zinc dust-acetic acid gave 4-alkyl-

phenylacetic acid. Condensation of **2a**, **2b** and **2c** with urea afforded 1,2-dihydro-5-(4-substituted phenyl)pyrimidin-2-one (**3a–3c**), which were converted to 2-chloropyrimidine derivatives (**4a–4c**) with phosphorous oxychloride. Alkylation of 4 with sodium alkoxide yielded the 5-(4-alkoxyphenyl)-2-alkoxypyrimidines (**5a–5f**) and 5-(4-alkylphenyl)-2-alkoxypyrimidines (**6a–6c**). 2-Alkylpyrimidines were obtained as described in Scheme II. The Vilsmeier reaction of 4-hydroxyphenylacetic acid and subsequent condensation with alkylamidines gave 5-(-hydroxyphenyl)-2-alkylpyrimidines (**9**). Alkylation of **9** with alkylbromide or alkyltosylate gave 5-(4-alkoxyphenyl)-2-alkylpyrimidines (**10a–10h**). The chiral materials were obtained from commercially available (S)-2-methylbutanol and (R)-citronellol.

RESULTS AND DISCUSSION

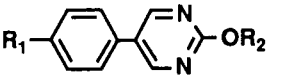
Melting and transition temperatures were measured with a polarizing microscope equipped with a heating stage and a differential scanning calorimeter (DSC). Identity of the mesophases was confirmed by examining the texture of a thin sample sandwiched between glass slides.[4] The melting and transition temperatures of homologous series 5, 6 and 10 are given in Table I and Table II. The mesomorphic ranges for these series are shown in Figure 1. The SA or SA-SC* combinations predominate in most homologs of these series and N* or high ordered smectic phases were not observed. As shown in Figure 1, the alkoxyl-alkyl compounds with relatively short chiral side chains (**6a**, **10a**, and **10f**) exhibit no mesophase, although the alkoxy-alkoxy compounds **5a** and **5f** exhibit the SA phase. In the case of medium length chiral chains, dialkoxy derivative (**5b**) showed SA and SC* mesophases, and the corresponding alkoxy-alkyl derivatives (**6b**, **10b** and **10g**) had only a SA phase. In the case of derivatives with relatively long chiral side chains, such as **5c**, **6c**, **10c** and **10h**, both dialkoxy and alkoxy-alkyl derivatives exhibited SA and SC* mesophases. Comparison of the clearing temperatures observed for the dialkoxy 5-phenylpyrimidines (5) with those for the analogous alkoxy-alkyl series (**6**, **10**) showed that the former series had a higher clearing temperature than the analogous series of **6** and **10** and that, accordingly, the thermal stabilities of the mesophase of the dialkoxy series were higher than those of the alkoxy-alkyl derivatives. Moreover, the mesomorphic range of the dialkoxy series (**5**) was wider than that of the alkoxy-alkyl series (**6**, **10**). This tendency of the mesophase more likely occurring in the dialkoxy series than in the alkoxy-alkyl series could be attributed to a dipole moment transverse to the molecular axis of the alkoxy group. This would have the effect of causing the mesophase.

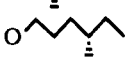
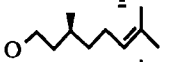
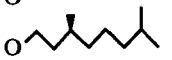
The homologous series which had (R)-citronellol or its dihydro derivative as a chiral part exhibited lower melting points and narrower mesomorphic ranges than the analogous series having a 6-methyloctyloxy side chain as a chiral part.

For the homologs **5c** and **10h**, the spontaneous polarizations (Ps) and optical response times (τ) were measured on 2 μm thick cells at a temperature 10°C below the upper limit of the SC* phase. The results are shown in Table III. Spontaneous polarizations were obtained by the triangular wave method[5] ($\pm$10 V, 200 Hz). Optical response times were obtained by applying a rectangular wave ($\pm$10 V, 200

TABLE I

Phase transition temperatures of homologous series **5** and **6**



Compound	R_1-	-OR_2	Phase transition temp.[a] Cr	Sc*	SA	Iso	m.p.[b]	c.p.[c]
5a	$C_{10}H_{21}O$-		• 37.5		• 66.0 •		63.0	69.0
5b	$C_{10}H_{21}O$-		• 39.0 •	57.5 •	80.0 •		63.0	82.0
5c	$C_{10}H_{21}O$-		• 53.5 •	76.0 •	84.1 •		77.0	86.0
5d	$C_{10}H_{21}O$-		• 28.0		• 44.0 •		41.0	45.0
5e	$C_{10}H_{21}O$-		• 30.0 •	37.0 •	54.0 •		45.0	58.0
5f	 O-	-$OC_{10}H_{21}$	• 59.0		• 63.0 •		82.0	
6a	C_8H_{17}-		• 32.0			•	58.0	
6b	C_8H_{17}-		• 47.1		• 52.5 •		51.8	55.0
6c	C_8H_{17}-		• 29.0 •	35.0 •	58.0 •		46.0	60.0

a) Phase transition temperatures were obtained on cooling at 5 ℃ /min.
b) melting point(℃)
c) clearing point(℃)

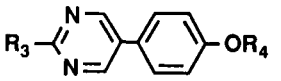
Hz) and were defined as the time difference between voltage reversal and a 90% change in optical transmission. The Ps values were very small, in agreement with a general rule that if the dipole is remote from the chiral center, the Ps value will be small.[6] Optical response times, however were very fast, and this could have been the effect of the very small rotational viscosity of 5-phenylpyrimidine derivatives.

EXPERIMENTAL

IR, ^{1}H NMR and mass spectra were recorded on a Shimazu 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 alcohol. The phase transition temperatures and melting points were determined using a Rigaku Denki DSC-8230 apparatus and texture observations were made using a Nikon XTP-II polarizing microscope in conjunction with a Mettler FP-82

TABLE II

Phase transition temperatures of homologous series 10



Compound	R_3-	-OR_4	Phase transition temp.[a] Cr	Sc*	SA	Iso	m.p.[b]	c.p.[c]
10a	$-C_8H_{17}$	-O	• 58.0			•	67.0	
10b	$-C_8H_{17}$	-O	• 39.0		• 61.0	•	51.0	66.0
10c	$-C_8H_{17}$	-O	• 36.0	• 48.0	• 68.0	•	40.0	72.0
10d	$-C_8H_{17}$	-O	• 20.0			•	20.0	
10e	$-C_8H_{17}$	-O	• 36.0			•	36.0	
10f	$-C_{12}H_{25}$	-O	• 51.2			•	65.0	
10g	$-C_{12}H_{25}$	-O	• 36.0		• 52.0	•	46.0	62.0
10h	$-C_{12}H_{25}$	-O	• 39.0	• 58.0	• 66.5	•	57.1	68.0

a) Phase transition temperatures were obtained on cooling at 5 ℃ /min.
b) melting point(℃)
c) clearing point(℃)

hot stage and FP-80 control unit. The some representative examples of the preparation of the compounds are given below.

3-Dimethylamino-2-(4-decyloxyphenyl)acroleine (**2a**). Phosphorous oxychloride (28 ml) was slowly added to a cooled dry DMF (30 ml) and the mixture was stirred for 30 min. A solution of 4-decyloxyphenylacetic acid (29.0 g) in dry DMF (120 ml) was slowly added to the above solution and then the mixture was heated at 50°C for 30 min, and subsequently at 70°C for 3 h. The reaction mixture was poured into water and neutralized with potassium carbonate (49.0 g). A solution of NaOH (100 g) in water (50 ml) was added to this solution and the mixture was heated at 50°C for 30 min. After cooling to room temperature, the reaction mixture was acidified with conc. HCl and extracted several times with ethyl acetate. The organic layers were collected, washed with water, dried over magnesium sulfate and condensed under reduced pressure. The solid residue was recrystallized from ether to yield **2a** (26.3 g).

IR (Nujol): 1640, 1605, 1585, 1510, 1270, 1235, 1200 cm^{-1} ^1H NMR ($CDCl_3$): δ 0.89 (3 h, *t*, *J* = 7 Hz), 1.13–2.00 (16 h, *m*), 2.83 (6 h, *s*), 3.95 (2 h, *t*, *J*= 7 Hz), 6.85 (2 h, *d*, *J* = 8 Hz), 7.08 (2 h, *d*, *J* = 8 Hz), 9.10 (1 h, *s*)

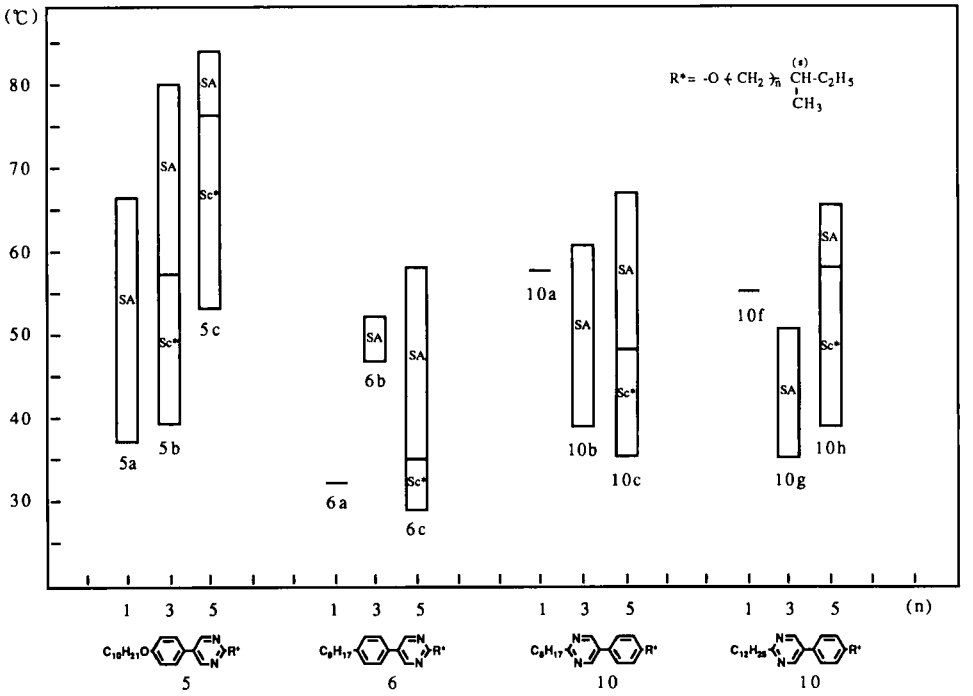


FIGURE 1 Mesomorphic ranges for the 5-phenylpyrimidine derivatives.

TABLE III

Spontaneous polarizations (Ps) and optical response times (τ) of compounds **5c** and **10h**[a]

Compound	Ps (nC/cm²)	τ (μ sec)
5c	<0.1	280
10h	<0.1	260

[a] Ps and τ were measured on 2 μm thick cells at a temperature 10°C below the upper limit of the Sc* phase.

1,2-Dihydro-5-(4-decyloxyphenyl)pyrimidin-2-one (**3a**). A solution of **2a** (6.62 g) and urea (1.5 g) in ethanol (60 ml) containing conc. HCl (2 ml) was refluxed for 16 h. After cooling to room temperature, the resulting precipitates were collected and recrystallized from ethanol to give 3a (3.9 g).
IR (Nujol): 1690, 1625, 1605, 1550, 1515 cm^{-1} ^1H NMR ($CDCl_3$): δ 0.87 (3 h, *m*), 0.80–1.90 (16 h, *m*), 4.00 (2 h, *t*, J = 7 Hz), 6.97 (2 h, *d*, J = 8 Hz), 7.35 (2 h, *d*, J = 8 Hz), 8.47 (2 h, *s*) Mass: *m/z* 328 (M^+)

2-Chloro-5-(4-decyloxyphenyl)pyrimidine (**4a**). To a solution of **3a** (3.3 g) in phosphorous oxychloride (7.0 ml) was added N,N′-diethylaniline (0.5 ml) and the mixture was heated at 110°C for 15 h. After cooling, the reaction mixture was poured into ice-water and extracted several times with ethyl acetate. The combined organic

layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was recrystallized from ethanol to yield **4a** (2.2 g).
IR (Nujol): 1600, 1570, 1535, 1510 cm^{-1} ^1H NMR ($CDCl_3$): δ 0.85 (3 h, *m*), 1.10–2.30 (16 h, *m*), 4.00 (2 h, *t*, *J* = 7 Hz), 7.02 (2 h, *d*, *J* = 9 Hz), 7.48 (2 h, *d*, *J* = 9 Hz), 8.80 (2 h, *s*)

(s)-2-(2-Methylbutyloxy)-5-(4-decyloxyphenyl)pyrimidine (**5a**). To an ice-cooled suspension of 60% sodium hydride (120 mg) in dry DMF (2.0 ml) was added (s)-methylbutanol (270 mg) and the mixture was stirred for 30 min. A solution of **4a** (700 mg) in dry DMF (3 ml) was added dropwise to the above mixture and the stirring was continued for 2 h at room temperature. The reaction mixture was poured into water and extracted several times with ether. The organic layers were collected, washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the resulting solid was purified by column chromatography on silica gel and recrystallized from methanol to give **5a** (470 mg).
IR (Nujol): 1590, 1545, 1520, 1465, 1445, 1375, 1330, 1290 cm^{-1} ^1H NMR ($CDCl_3$): δ 1.00 (3 h, *t*, *J* = 6 Hz), 1.09 (3 h, *t*, *J* = 7 Hz), 0.80–2.10 (22 h, *m*), 3.99 (2 h, *t*, *J* = 6 Hz), 4.20 (1 h, *d*, *J* = 6 Hz), 4.24 (1 h, *d*, *J* = 6 Hz), 6.98 (2 h, *d*, *J* = 8 Hz), 7.41 (2 h, *d*, *J* = 8 Hz), 8.64 (2 h, *s*) Mass: *m/z* 398 (M^+)

3-Dimethylamino-2-(4-hydroxyphenyl)acroleine (**8**). 8 was prepared in the same way as **2a** and gave 41.9% yield.
IR (Nujol): 3100, 1630, 1610, 1550, 1510 cm^{-1} ^1H NMR ($CDCl_3$): δ 2.27 (6 h, *s*), 7.02 (2 h, *d*, *J* = 9 Hz), 7.04 (1 h, *s*), 7.21 (2 h, *d*, *J* = 9 Hz), 8.97 (1 h, *s*), 9.25 (1 h, *s*) Mass: *m/z* 191 (M^+)

2-Octyl-5-(4-hydroxyphenyl)pyrimidine (**9a**). A solution of 8 (380 mg) and nonylamidine (340 mg) in pyridine (2 ml) was heated at 70°C for 5 h. The cooled reaction mixture was poured into water, acidified with dilute HCl and extracted several times with ether. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with hexane-ether as eluent to yield **9a** (350 mg)
IR (Nujol): 1610, 1580, 1540, 1510 cm^{-1} ^1H NMR ($CDCl_3$): δ 0.82 (3 h, *m*), 0.60–2.10 (12 h, *m*), 3.00 (3 h, *t*, *J* = 8 Hz), 6.93 (2 h, *d*, *J* = 8 Hz), 7.30 (2 h, *d*, *J* = 8 Hz), 8.83 (2 h, *s*) Mass: *m/z*/ 284 (M^+)

(s)-2-Octyl-5-[4-(6-methyloctyloxy)phenyl]pyrimidine (**10c**). To an ice-cooled suspension of 60% sodium hydride (36 mg) in dry DMF (3 ml) was added a solution of **9a** (210 mg) in dry DMF (5 ml). After stirring for 30 min, (S)-6-methyloctyloxy-*p*-toluenesulfonate (540 mg) was added dropwise and the mixture was stirred for 2 h at room temperature and then heated at 50°C for 30 min. After cooling, the reaction mixture was poured into water and extracted several times with ether. The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the resulting solid was purified

by column chromatography on silica gel with hexane-ether as eluent followed by recrystallization from methanol to yield **10c** (265 mg).
IR (Nujol): 1605, 1580, 1530, 1510, 1425, 1280 cm^{-1} ^1H NMR ($CDCl_3$): δ 0.83 (3 H, *m*), 0.70–2.10 (29 H, *m*), 3.00 (2 H, *t*, J = 7 Hz), 4.02 (2 H, *t*, J = 7 Hz), 7.01 (2 h, *d*, J = 8 Hz), 7.51 (2 H, *d*, J = 8 Hz), 8.84 (2 H, *s*) Mass: *m/z* 410 (M^+)

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