Synthesis and Mesomorphic Properties of 5-[4-(Alkyloxy)phenyl]-2-{4'-[(S)-2-methylbutyl]phenyl}pyrimidine

Seung-Un Park,* Chan-Jae Lee, and Jin Hee Han

*Department of Chemistry, Konkuk University, Seoul 143-701, Korea. *E-mail: psupark@konkuk.ac.kr*
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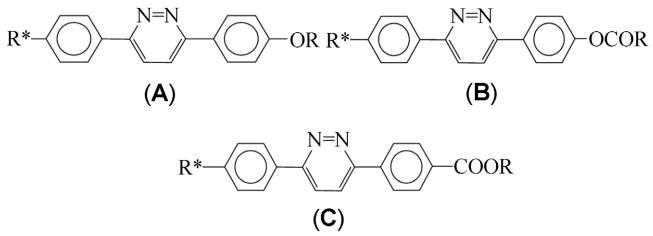
In recent decades the display techniques using liquid crystal compounds have been greatly advanced and become prevalent in our daily life. In particular, since the discovery of ferroelectric smectic C* liquid crystals by Meyer,[1] the concept of the ferroelectric liquid crystals has much accelerated the synthesis and the engineering of those material.[2] Now their theoretical, physicochemical and electro-optical properties for the practical applications are rather well documented.[3] Even if, to the organic chemists point of view, the structure-property relationship in this field has been the first choice to be studied, however, the accurate prediction of properties for a new compound is not possible yet.

In this context we had particularly studied the structure-mesomorphic property relationship of the liquid crystals, such as **A**, **B** and **C**, with diarylpyridazine core and terminal units of a chiral R* and a long chain R, as shown below. Herein the chiral mesogen R*, (S)-2-methylbutyl, and alkyl chains of 6-12 carbons were used as terminal units.



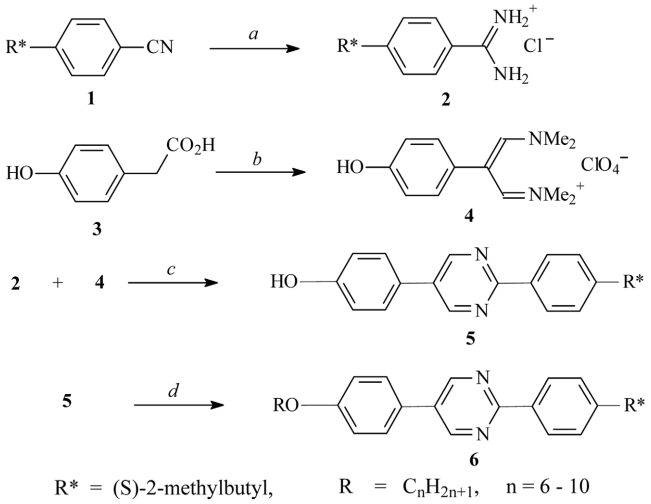
(**A**) (**B**) (**C**)

In the alkoxy compound (**A**) cases neither smectic A(SmA) nor nematic(N) was observed. Along with a few unidentified mesophases the Smectic C*(SmC*) mesophases were observed in the 176-207 °C ranges for hexyl, and 143-197 °C ranges for dodecyl, respectively.[4] The mesomorphic behaviors of the acyloxy compound (**B**) were very similar to those of compound (**A**), which showed only the SmC* mesophases, and neither SmA nor N. The temperature ranges of those SmC* mesophases were 192-205 °C for hexyl, and 189-204 °C for undecyl, respectively.[5] However, in the alkyloxycarbonyl compound (**C**) neither the nemetic nor SmC* mesophases were observed, instead the SmA mesophases were the only observed. The temperature ranges of those SmA mesophases were 156-179 °C for hexyl, and 143-168 °C for dodecyl, respectively.[5]

Now we wish to report the short synthesis and the mesomorphic behaviors of the pyrimidine core liquid crystals with (S)-2-methylbutyl and alkyl chains of 6-10 carbons as terminal units. In the synthesis shown in Scheme 1 we needed 4-[(S)-2-methylbutyl]phenylamidine hydrochloride (**2**) and 1-dimethylamino-3-dimethylimino-2-(4-hydroxyphenyl)propene perchlorate (**4**) as key intermediates.

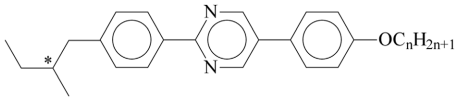
The amidine hydrochloride compound (**2**) was prepared in 74% overall from the Pinner reaction of the 4-((S)-2-methylbutyl)benzonitrile[6] (**1**) with ethanolic HCl at 0 °C in benzene followed by the treatment of the imidate ester with saturated ammonia in ethanol at room temperature for 50 h.[7] The yellow crystalline trimethinium perchlorate (**4**) was in 82% overall prepared from the Vilsmeier-Haack reaction of the hydroxyphenylacetic acid (**3**) with $POCl_3$ in dimethylformamide at −10 °C for 1 h, then heating to 80 °C for 7 h, followed by the treatment with 70% $HClO_4$ at −10 °C.[8] Reaction of **2** with **4** in pyridine at 80 °C for 8 h gave the compound **5** in 95% yield. Reactions of **5** with 1-bromalkanes in the presence of K_2CO_3 in refluxing acetone for 5 h gave the desired 2,5-diaryl pyrimidine compounds **6** in 61-84%.[9]

We had examined the mesomorphic properties of 5-[4-(alkyloxy)phenyl]-2-{4-[(S)-2-methylbutyl]phenyl}pyrimidine compounds (**6**) using a Nikon Labophot-pol polarizing



Scheme 1. Reagents and conditions: *a*; i) **1** (0.025 mol) in 6.4 mL PhH, sat. HCl(g) in 5.1 mL ethanol, 0 °C, 70 h. ii) 14% NH_3/ethanol, rt, 50 h, overall 74%. *b*; i) DMF, 0 °C, $POCl_3$ (0.19 mol), then −10 °C, **3** (0.066 mol) 50 min addition, then 80 °C, 7 h. ii) 70% $HClO_4$ (20 mL), −10 °C, overall 82%, *c*; **2** (1.52 mmol), **4** (1.8 mmol) in 4.5 mL pyridine, 80 °C, 8 h, 95%. *d*; 5 (1.87 mmol), 1-bromohexane (1.88 mmol) and K_2CO_3 (0.52 g) in 10 mL acetone, reflux 5 h, 84%.[9]

Table 1. Phase Transition Temperatures and Phase Transition of 5-[4-(Alkyloxy)phenyl]-2-{4'-[(S)-2-methylbutyl]phenyl} pyrimidine (**6**)



C_nH_{2n+1}	Phase Transition[a] and Transition Temperature[b] (°C)					
a: n = 6	CrK	72.8(8.03)	SmX 140.1(3.05)	SmC* 153.4(0.83)	SmA 178.3(3.45)	I
b: n = 7	CrK	78.8(7.27)	SmX 117.4(1.42)	SmC* 153.4(0.59)	SmA 174.2(3.37)	I
c: n = 8	CrK	84.6(6.30)	SmX 103.9(0.28)[c]	SmC* 149.9(0.30)	SmA 173.2(3.58)	I
d: n = 9	CrK	86.6(7.49)	SmX 102.6(0.37)	SmC* 151.5(0.19)	SmA 171.9(4.36)	I
e: n = 10	CrK	86.4(6.13)	SmX 98.4(0.34)	SmC* 150.4(0.16)	SmA 170.3(3.60)	I

[a]Classified by the observed microscopic texture on cooling the isotropic phase using Nikon Labophot-pol polarizing microscope equipped with a heating stage. [b]Temperature measured by Dupont 9900 DSC on heating 3 mg sample in 2°/min; enthalpy (kJ/mol) in parenthesis. [c]An additional metastable phase transition was observed at 97.89 °C (0.23 kJ/mol) for n = 8.

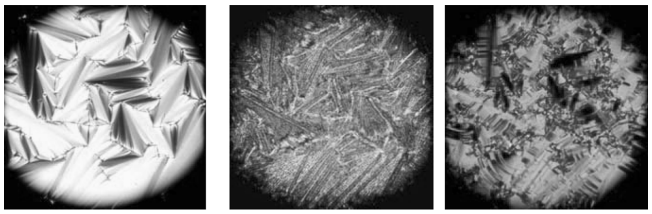


Figure 1. Photographs of mesomorphic textures of decyloxy derivative (**6e**) on cooling from the isotropic with exactly the same viewing area of the sample and taken at temperature: (I) 160 °C; SmA, (II) 110 °C; broken texture of SmC*, (III) 85 °C; SmX.

microscope (× 150) equipped with a heating stage by either heating the crystals phases or cooling the isotropic phases, and measured the phase transition temperatures and enthalpies using a Dupont 9900 DSC. The results are summarized in Table 1.

In contrast with the pyridazine analogue (**A**) the synthesized pyrimidine analogues (**6**) had three mesophases between crystal and isotropic phase. On the basis of the microscopic observations and DSC measurements the two mesophases could be identified as SmA*, SmC*.[10] Even if the third mesophase was clearly present and could be photographed as shown in Figure 1, however, its phase identification was uncertain at this moment, thus, it was tentatively designated as SmX. As seen in pyridazine analogues,[4] the longer the terminal alkyl units, the temperatures for the crystal to mesophase increased, and those for the mesophase to isotropic decreased.

In summary the synthesis of 2,5-diarylpyrimidine derivatives with alkoxy (C_nH_{2n+1}, n = 6, 7, 8, 9, and 10) and (S)-2-methylbutyl as terminal units were performed from the pyrimidine formation reaction of 1-dimethylamino-3-dimethylimino-2-(4-hydroxyphenyl)propene perchlorate and 4-((S)-2-methylbutyl)phenylamidine hydrochloride followed by the alkylation of the intermediate. The microscopic observation and DSC measurement of the phase transition revealed those synthesized compounds clearly to have Smectic A* and Smectic C* mesophases.

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9. Yields of **6**: **6a**, 84%; **6b**, 80%; **6c**, 74%; **6d**, 73%; **6e**, 65%; n-Dode- cyloxy, 61%. A representative ^{1}H-NMR (400 MHz, $CDCl_3$): **6a**; 84%, δ0.7-1.1 (9H, m), δ1.3 (8H, m), δ1.7 (2H, m), δ2.0 (1H, m), δ2.32 (1H, dd, J = 10 Hz, J = 10 Hz), δ2.68 (1H, dd, J = 10 Hz, J = 7 Hz), δ3.95 (2H, t, J = 8 Hz), δ6.83 (2H, d, J = 8.2 Hz), 7.18 (2H, d, J = 7.8 Hz), 7.37 (2H, d, J = 8.2 Hz), 7.43 (2H, d, J = 7.8 Hz), δ8.90 (2H, s).
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