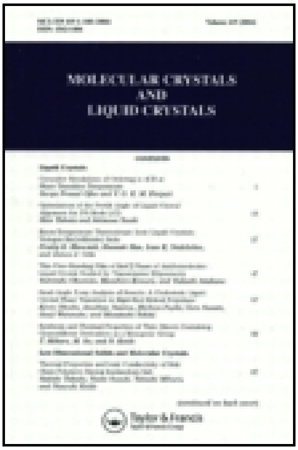

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Synthesis of Liquid Crystals with Bent-Rod Structure: Mesogenic Thiazole Derivatives with Long Alkoxyl Chains

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Synthesis of Liquid Crystals with Bent-Rod Structure: Mesogenic Thiazole Derivatives with Long Alkoxyl Chains

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Liquid-crystalline 2,5-diarylethynylthiazole derivatives with bent-rod structure were prepared by a palladium-catalyzed cross-coupling reaction. The 2,5-diarylethynylthiazole derivatives prepared in the present study exhibit the smectic A and nematic phases.

Keywords: bent-rod structure; cross-coupling reaction; 2,5-diarylethynylthiazole; liquid crystals; nematic phase

INTRODUCTION

Recently there has been considerable interest in heterocyclic molecules due to their diversified molecular design and remarkable optical [1–3], liquid-crystalline [4], and electronic properities [5]. Especially, bent-rod structures have received considerable attention due to the discovery of a new class of achiral ferroelectric liquid crystal [6a]. While these materials are still under investigation, there is the possibility that molecules in a given domain spontaneously adopt a single chiral conformation [6]. While the structures and interactions necessary to creat stable liquid-crystalline phases from bent-rod systems are not fully understood, it has been generally found that materials with severely bent structures display liquid-crystalline phases with lower thermodynamic stability than their straight-rod relatives [7h].

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Typically, bent-core molecules incorporate at least one Schiff-base unit. Therefore, a major drawback of these compounds is their limited thermal, hydrolytic, and photochemical stability. Furthermore, in most cases, these mesophases occur at rather high temperatures. Therefore, the design of novel, stable and low-melting bent-core liquid crystals without a sensitive Schiff-base unit is a topical subject in liquid crystal research. To produce a bent-rod structure with good prospects for liquid crystallinity, we have decided to synthesize materials with a thiazole as a central element of the mesogen. A 2,5-disubstituted thiazole moiety exhibits a larger angle (154°) than other logical building blocks (154° for 2,5-disubstituted thiophene, 143° for 2,5-disubstituted furan, 141° for 2,5-disubstituted pyrrole, and 120° for 1,3-disubstituted benzene) [7b]. Some liquid crystals with bent-rod structures having mesogenic units other than the thiazole-2,5-diyl unit were previously reported [7].

Here we report a new class of liquid-crystalline thiazole derivative **1** with bent-rod structure and properties.

RESULTS AND DISCUSSION

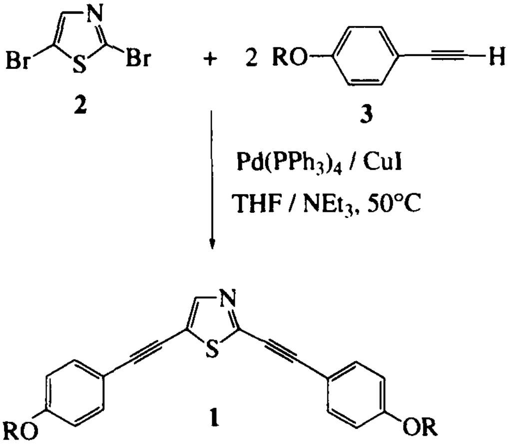
The synthetic access of the thiazole derivative **1** is possible due to the development of a palladium-catalyzed carbon-carbon cross-coupling reaction [8–10] of terminal alkynes having long alkoxyl groups with 2,5-dibromothiazole **2**. Terminal alkyne **3** having long alkoxyl groups were prepared in three steps from 4-hydroxyacetophenone as previously reported [11].

TABLE 1 Yields of 2,5-diarylethynylthiazole derivative 1[a]

compound	*2,5-diarylethynylthiazole derivative 1 (isolated yield, %)*
1a	87
1b	87
1c	86
1d	86
1e	86
1f	85

a. Typical conditions: 2,5-dibromothioazole (0.3 mmol), terminal alkyne (0.62 mmol), $Pd(PPh_3)_4$ (0.03 mmol), CuI (0.03 mmol), NEt_3 (0.8 ml), THF (8 ml), 50 °C, 8 h.

The compounds **1a-f** were synthesized by a Pd (0)/Cu (I)-catalyzed coupling reaction of the corresponding terminal alkyne **3** having long alkoxyl groups with 2,5-dibromothiazole **2** at 50 °C in THF/NEt_3 as shown in Scheme 1. 2,5-Diarylethynylthiazole **1a** was formed in an 87% yield. Other 2,5-diarylethynylthiazole derivatives **1b-f** were obtained by this procedure in 85–87%. The results are summarized in Table I. Table I indicates that the synthesis of the 2,5-diarylethynylthiazole derivatives proceeds well even in the case of the substrates bearing long alkoxyl groups and the yield is not affected by alkoxyl groups. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures. Compounds **1a-f** are air-stable solid that can be stored at ambient temperature for prolonged periods of time.

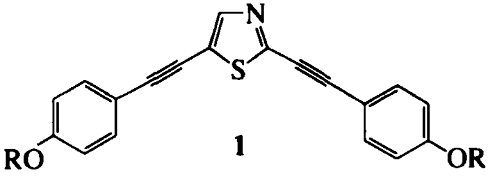


1a R = (*S*)-$C_2H_5C^*H(CH_3)CH_2$
1b R = *n*-C_6H_{13}
1c R = *n*-C_8H_{17}
1d R = *n*-$C_{10}H_{21}$
1e R = *n*-$C_{12}H_{25}$
1f R = *n*-$C_{14}H_{29}$

SCHEME 1 Synthesis of thiazole derivative **1** having long alkoxyl groups

Mesogenic properties of the thiazole derivatives

All the thiazole compounds **1a-f** showed mesogenic properties. The mesogenic properties of the obtained compounds were investigated by polarized optical microscopy (POM) on a hot stage and differential scanning calorimetry (DSC). The heating and cooling rates were 5 °C/min. The DSC thermograms of compounds **1a-f** were measured by heating and subsequent cooling. The results are summarized in Table II. All the 2,5-diarylethynylthiazoles having long alkoxyl



1

FIGURE 1 Bent-rod structure of thiazole derivative 1

groups behave as enantiotropic liquid crystals. The appearance of the mesogenic properties of the compounds **1b-f** strongly depends on the length of the alkoxyl groups. In Figure 2, the dependence of the mesomorphic properties of the homologous series of the alkylsubstituted compounds **1b-f** (n = 6, 8, 10, 12, and 14) on the chain length is shown schematically. The compounds **1b**, **1c**, **1d**, and **1e** exhibited only the nematic phase with Schlieren texture when viewing the samples through the POM. Compound **1f**, however, displayed the enantiotropic smectic A and nematic phases.

TABLE II Liquid crystal phase and transition temperatures of 2,5-diarylethynylthiazole derivative 1

compound	*R*	*phase transition temperature (°C)^a*
1a	$(S)\text{-}C_2H_5C^*H(CH_3)CH_2O$	$K \xrightarrow{94.3} I$ $K \xleftarrow{76.3} S_C^* \xleftarrow{76.7} I$
1b	$n\text{-}C_6H_{13}O$	$K \underset{73.1}{\overset{85.5}{\rightleftharpoons}} N \underset{139.5}{\overset{141.5}{\rightleftharpoons}} I$
1c	$n\text{-}C_8H_{17}O$	$K \underset{72.0}{\overset{86.0}{\rightleftharpoons}} N \underset{132.0}{\overset{134.5}{\rightleftharpoons}} I$
1d	$n\text{-}C_{10}H_{21}O$	$K \underset{70.9}{\overset{86.6}{\rightleftharpoons}} N \underset{125.4}{\overset{127.0}{\rightleftharpoons}} I$
1e	$n\text{-}C_{12}H_{25}O$	$K \xrightarrow{89.8} N \underset{120.4}{\overset{122.5}{\rightleftharpoons}} I$ $K \xleftarrow{77.3} S_A \xleftarrow{85.5} N$
1f	$n\text{-}C_{14}H_{29}O$	$K \underset{78.9}{\overset{86.1}{\rightleftharpoons}} S_A \underset{105.3}{\overset{107.9}{\rightleftharpoons}} N \underset{120.3}{\overset{121.9}{\rightleftharpoons}} I$

a. K, crystal; S_A, smectic A; N, nematic; S_C^*, chiral smectic C; I, isotropic

Most importantly, a chiral smectic C phase was observed with the 2,5-diarylethynylthiazole **1a**, which showed the characteristic striated fan-shaped texture.

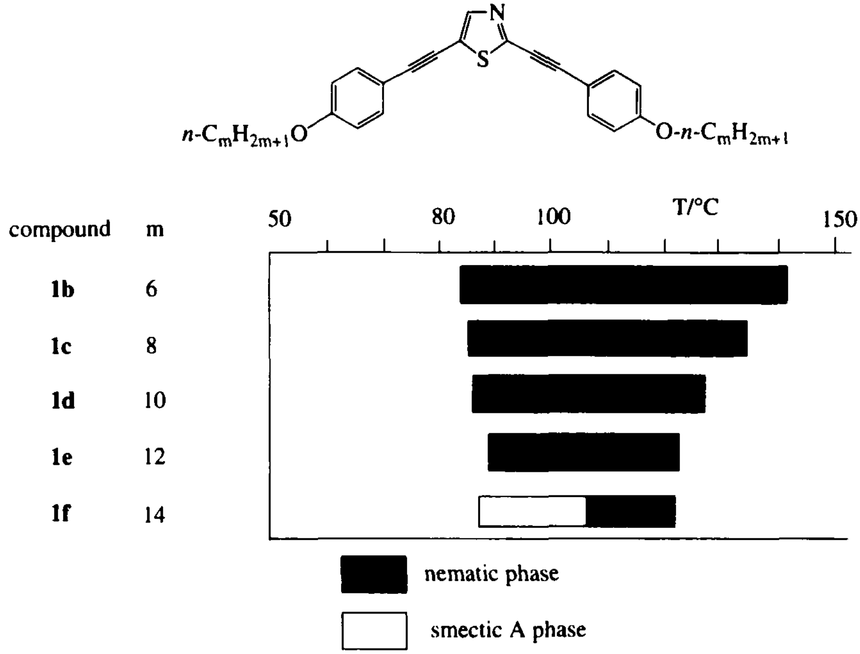


FIGURE 2 Transition temperatures of the homologous series of compounds **1b-f**

CONCLUSION

We synthesized a new class of 2,5-diarylethynylthiazole derivative **1a-f** which has long alkoxyl groups and a bent-rod structure without the unstable Schiff-base unit. These compounds behave as liquid-crystalline materials. We suggest that these novel and stable materials can be used for various future applications such as nonlinear optical and liquid crystal display devices.

EXPERIMENTAL

General

^{1}H NMR spectra were obtained with a JEOL JNM-LA 300 (300 MHz) spectrometer. Chemical shifts are given in ppm. Elemental analyses were carried out with a Yamagimoto CHN Autocoder, Type MT-2. IR spectra were recorded on a JASCO IR-810 spectrometer with KBr pellets. The transition temperatures were determined by a polarizing microscope (OLYMPUS, BHSP) equipped with a hot stage and a controller (JAPAN HYTECH, TH-600RH) and also on the basis of the thermograms recorded on a differential scanning calorimeter (RIGAKU, THERMOFLEX, DSC 8230).

General Procedure for Synthesis of the 2,5-Diarylethynylthiazole Derivatives 1

All new compounds showed satisfactory spectroscopic and analytical data.

Typical procedure for product **1e**: A mixture of 2,5-dibromothiazole **2** (72.9 mg, 0.3 mmol), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), 4-dodecyloxyphenylacetylene (**3e**) (177.5 mg, 0.62 mmol), freshly distilled triethylamine (0.8 ml) and anhydrous THF (8 ml) was degassed and stirred at 50°C for 8 h under argon. After cooling to room temperature, the mixture was evaporated, washed with saturated aqueous NH_4Cl, and extracted with chloroform. The combined extracts were washed with water and brine, and then dried over anhydrous Na_2SO_4 and evaporated. The product was purified by silica gel column chromatography, using chloroform as the eluent, and recrystallized (EtOH 100%) to afford a pale yellow powder of pure **1e** in 86% yield.

2,5-Bis[[((S)-4-(3-methyl)butyloxyphenyl)ethynyl]]thiazole (1a)

^1H NMR (300 MHz, $CDCl_3$) $\delta = 0.93 - 1.03$ (m, 12 H, CH_3), 1.25 – 1.57 (m, 4 H, CH_2), 1.80 – 1.88 (m, 2 H, CH), 3.74 – 3.87 (m, 4 H, OCH_2), 6.87 (d, 2 H, *J* 2.6 Hz, ArH), 6.91 (d, 2 H, *J* 2.6 Hz, ArH), 7.44 (d, 2 H, *J* 8.8 Hz, ArH), 7.53 (d, 2 H, *J* 8.8 Hz, ArH), 7.88 (s, 1 H, thiazole). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{29}H_{31}NO_2S$: C, 76.15; H, 6.78; N, 3.06; S, 7.01, Found: C, 75.90; H, 6.86; N, 3.22; S, 7.23.

2,5-Bis[(4-hexyloxyphenyl)ethynyl]thiazole (1b)

^1H NMR (300 MHz, $CDCl_3$) $\delta = 0.89$ (t, 6 H *J* 6.4 Hz, CH_3), 1.32 (br s, 12 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.86 (d, 2 H, *J* 2.6 Hz, ArH), 6.89 (d, 2 H, *J* 2.6 Hz, ArH), 7.46 (d, 2 H, *J* 8.8 Hz, ArH), 7.52 (d, 2 H, *J* 8.8 Hz, ArH), 7.88 (s, 1 H, thiazole). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{31}H_{35}NO_2S$: C, 76.71; H, 7.21; N, 2.88; S, 6.61. Found: C, 76.88; H, 7.30; N, 2.82; S, 6.32.

2,5-Bis[(4-octyloxyphenyl)ethynyl]thiazole (1c)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.89$ (t, 6 H *J* 6.4 Hz, CH_3), 1.32 (br s, 20 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.86 (d, 2 H, *J* 2.6 Hz, ArH), 6.90 (d, 2 H, *J* 2.6 Hz, ArH), 7.43 (d, 2 H, *J* 8.8 Hz, ArH), 7.51 (d, 2 H, *J* 8.8 Hz, ArH), 7.88 (s, 1 H, thiazole). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{35}H_{43}NO_2S$: C, 77.64; H, 7.94; N, 2.59; S, 5.92. Found: C, 77.52; H, 7.80; N, 2.43; S, 5.76.

2,5-Bis[(4-decyloxyphenyl)ethynyl]thiazole (1d)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.89$ (t, 6 H *J* 6.4 Hz, CH_3), 1.28 (br s, 28 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.82 (d, 2 H, *J* 2.6 Hz, ArH), 6.90 (d, 2 H, *J* 2.6 Hz, ArH), 7.46 (d, 2 H, *J* 8.8 Hz, ArH), 7.53 (d, 2 H, *J* 8.8 Hz, ArH), 7.88 (s, 1 H, thiazole). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{39}H_{51}NO_2S$: C, 78.40; H, 8.54; N, 2.34; S, 5.37. Found: C, 78.22; H, 8.50; N, 2.43; S, 5.26.

2,5-Bis[(4-dodecyloxyphenyl)ethynyl]thiazole (1e)

1H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6 H *J* 6.4 Hz, CH_3), 1.28 (br s, 36 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 3.98 (t, 4 H, *J*6.4 Hz, OCH_2), 6.86 (d, 2 H, *J* 2.6 Hz, ArH), 6.90 (d, 2 H, *J* 2.6 Hz, ArH), 7.45 (d, 2 H, *J* 8.8 Hz, ArH), 7.53 (d, 2 H, *J*8.8 Hz, ArH), 7.88 (s, 1 H, thiazole). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{43}H_{59}NO_2S$: C, 79.03; H, 9.03; N, 2.14; S, 4.91. Found: C, 78.97; H, 8.90; N, 2.22; S, 4.65.

2,5-Bis[(4-tetradecyloxyphenyl)ethynyl]thiazole (1f)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6 H *J* 6.4 Hz, CH_3), 1.28 (br s, 44 H, CH_2), 1.77 (quint, 4 H, *J* 6.8 Hz, CH_2), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.86 (d, 2 H, *J* 2.6 Hz, ArH), 6.90 (d, 2 H, *J* 2.6 Hz, ArH), 7.45 (d, 2 H, *J* 8.8 Hz, ArH), 7.51 (d, 2 H, *J* 8.8 Hz, ArH), 7.88 (s, 1 H, thiazole). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{47}H_{67}NO_2S$: C, 79.56; H, 9.44; N, 1.97; S, 4.52. Found: C, 79.39; H, 9.37; N, 2.21; S, 4.32.

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