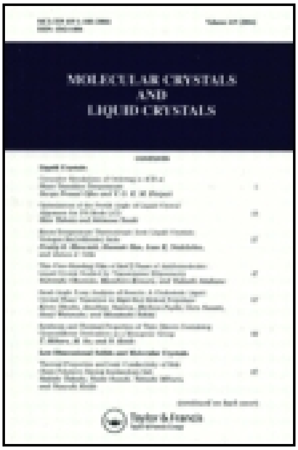

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Synthesis of Liquid Crystals with Bent-Rod Structure: 4-Methylthiazole Derivatives with Nematic Phase

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Synthesis of Liquid Crystals with Bent-Rod Structure: 4-Methylthiazole Derivatives with Nematic Phase

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Liquid-crystalline 2,5-diarylethynyl-4-methylthiazole derivatives with bent-rod structures were prepared by a palladium-catalyzed cross-coupling reaction. The 2,5-diarylethynyl-4-methylthiazole derivatives prepared in the present study exhibit only the nematic phase.

Keywords: bent-rod structure; cross-coupling reaction; 2,5-diarylethynyl-4-methylthiazole; liquid crystals; nematic phase

INTRODUCTION

Recently much attention has been paid to the synthesis and properties of molecules containing the thiazole unit [1, 2], since these molecules are useful for applications in several fields. π-conjugated polymers bearing thiazole units were found to serve as a unique electrically conducting polymer [3].

However, despite their high potential utility as materials for various purposes, liquid crystals having a thiazole unit have not been reported thus far. We have previously reported an efficient synthesis of thiazole derivatives with long alkoxyl groups by a palladium-catalyzed cross-coupling reaction [4].

The simplest and most technologically important liquid crystal phase is the nematic phase because of its rapid response to electric and magnetic fields [5]. Especially, bent-rod structures have received considerable attention due to the discovery of a new class of achiral ferroelectric liquid crystal [5a]. While these

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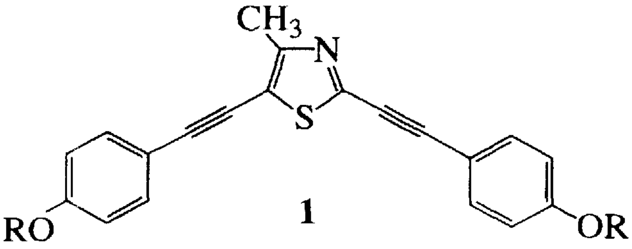
materials are still under investigation, there is the possibility that molecules in a given domain spontaneously adopt a single chiral conformation [5]. While the structures and interactions necessary to create stable liquid-crystalline phases from bent-rod systems are not fully understood, it has been generally found that materials with severely bent structures display liquid-crystalline phases with lower thermodynamic stability than their straight-rod relatives [6h].

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 4-methylthiazole 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) [6b]. Some liquid crystals with bent-rod structures having mesogenic units other than the thiazole-2,5-diyl unit were previously reported [6].

Here we report a new class of liquid-crystalline 4-methylthiazole derivative **1** with a bent-rod structure and properties. By introducing the methyl group into the thiazole unit, the phase transition temperature of the previously reported thiazole-based liquid-crystalline materials [4] is considerably lowered.



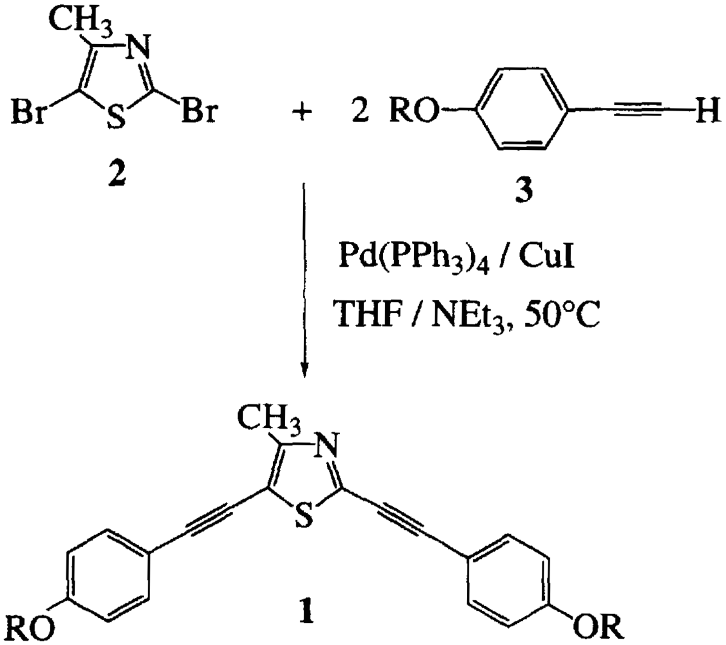
1

FIGURE 1 Bent-rod structure of 4-methylthiazole derivative 1

RESULTS AND DISCUSSION

The synthetic access of the 4-methylthiazole derivative **1** is possible due to the development of a palladium-catalyzed carbon-carbon cross-coupling reaction

[7–9] of terminal alkynes having long alkoxyl groups with 2,5-dibromo-4-methylthiazole **2**. Terminal alkyne **3** having long alkoxyl groups were prepared in three steps from 4-hydroxyacetophenone as previously reported [10].



1a R = n-C_8H_{17}
1b R = n-$C_{10}H_{21}$
1c R = n-$C_{12}H_{25}$
1d R = n-$C_{14}H_{29}$
1e R = n-$C_{16}H_{33}$

SCHEME 1 Synthesis of 4-methylthiazole derivative **1** having long alkoxyl groups

The compounds **1a-e** were synthesized by a Pd (0)/Cu (I)-catalyzed coupling reaction of the corresponding terminal alkyne **3** having long alkoxyl groups with 2,5-dibromo-4-methylthiazole **2** at 50°C in THF/NEt_3 as shown in Scheme 1. 2,5-Bis[(4-octyloxyphenyl)ethynyl]-4-methylthiazole **1a** was formed in an 83% yield. Other 2,5-diarylethynyl-4-methylthiazole derivatives **1b-e** were obtained by this procedure in 83–86%. The results are summarized in Table I. Table I indicates that the synthesis of the 2,5-diarylethynyl-4-methylthiazole 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-e** are air-stable solid that can be stored at ambient temperature for prolonged periods of time.

TABLE I Yields of 2,5-diarylethynyl-4-methylthiazole derivative 1[a]

compound	*2,5-diarylethynyl-4-methylthiazole derivative 1 (isolated yield, %)*
1a	83
1b	83
1c	85
1d	83
1e	86

[a] Typical conditions: 2,5-dibromo-4-methylthioazole (0.30 mmol), terminal alkynes (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.

Mesogenic properties of the 4-methylthiazole derivatives

All the 4-methylthiazole 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 by differential scanning calorimetry (DSC). The heating and cooling rates were 5 °C/min. The DSC thermograms of compounds **1a-e** were measured by heating and subsequent cooling. The results are summarized in Table II. All the 2,5-diarylethynyl-4-methylthiazoles having long alkoxyl groups behave as enantiotropic liquid crystals. In the case of the previously reported 2,5-diarylethynylthiazole derivatives [4], their phase transition temperatures were higher than 2,5-diarylethynyl-4-methylthiazole derivatives **1a-e** by 25–40°C. For the tetradecyloxy compound of thiazole, the smectic A phase was observed [4], however, for the tetradecyloxy compound of 4-methylthiazole, such a smectic A phase was not observed and only the nematic phase was observed. The reason for the lowering of the phase transition temperatures can be explained by a weakening of the molecular cooperative packing by introduction of the methyl group in the thiazole core. Compounds **1a-d** particularly had a wide liquid-crystalline temperature range and their transition temperatures were lower than the other compound **1e**. Compounds **1a-e** exhibited only the nematic phase with Schlieren texture when viewing the samples through the POM.

TABLE II Liquid crystal phase and transition temperatures of 2,5-diarylethynyl-4-methylthiazole derivative **1**

compound	*R*	*phase transition temperature (°C)*[a]
1a	n-$C_8H_{17}O$	$K \underset{40.0}{\overset{61.3}{\rightleftharpoons}} N \underset{92.9}{\overset{93.5}{\rightleftharpoons}} I$
1b	n-$C_{10}H_{21}O$	$K \underset{37.3}{\overset{44.2}{\rightleftharpoons}} N \underset{90.5}{\overset{91.5}{\rightleftharpoons}} I$
1c	n-$C_{12}H_{25}O$	$K \underset{38.7}{\overset{57.4}{\rightleftharpoons}} N \underset{77.3}{\overset{95.1}{\rightleftharpoons}} I$
1d	n-$C_{14}H_{29}O$	$K \underset{39.5}{\overset{67.4}{\rightleftharpoons}} N \underset{85.7}{\overset{87.9}{\rightleftharpoons}} I$
1e	n-$C_{16}H_{33}O$	$K \underset{55.4}{\overset{65.9}{\rightleftharpoons}} N \underset{73.8}{\overset{73.4}{\rightleftharpoons}} I$

[a] K, crystal; N, nematic; I, isotropic.

CONCLUSION

We have synthesized a new class of 2,5-diarylethynyl-4-methylthiazole derivatives **1a-e** which have 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 useful for various future applications such as nonlinear optical and liquid crystal display devices. Syntheses of the starting materials (**2** [3] and **3** [10]) of the liquid-crystalline compounds have been well established and are not difficult.

EXPERIMENTAL

General

^1H 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 Yanagimoto 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-Diarylethynyl-4-methylthiazole

Derivatives 1

All new compounds showed satisfactory spectroscopic and analytical data.

Typical procedure for product **1a**: A mixture of 2,5-dibromo-4-methylthiazole **2** (77.0 mg, 0.3 mmol), $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol), CuI (5.7 mg, 0.03 mmol), 4-octyloxyphenylacetylene (**3a**) (142.7 mg, 0.62 mmol), freshly distilled triethylamine (1.0 ml) and anhydrous THF (10 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/ethylacetate = 3/1) to afford a yellow powder of pure **1a** in 83% yield.

2,5-Bis[(4-octyloxyphenyl)ethynyl]-4-methylthiazole (1a)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6 H *J* 6.4 Hz, CH_3), 1.26 (br s, 20 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 2.56 (s, 3 H, CH_3), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.87 (d, 4 H, *J* 8.6 Hz, ArH), 7.44 (d, 2 H, *J* 8.4 Hz, ArH), 7.50 (d, 2 H, *J* 8.4 Hz, ArH). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{36}H_{45}NO_2S$: C, 77.84; H, 8.10; N, 2.52; S, 5.77. Found: C, 77.74; H, 8.12; N, 2.51; S, 5.86.

2,5-Bis[(4-decyloxyphenyl)ethynyl]-4-methylthiazole (1b)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (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), 2.56 (s, 3 H, CH_3), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.88 (d, 4 H, *J* 8.6 Hz, ArH), 7.44 (d, 2 H, *J* 8.4 Hz, ArH), 7.50 (d, 2 H, *J* 8.4 Hz, ArH). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{40}H_{53}NO_2S$: C, 78.57; H, 8.67; N, 2.29; S, 5.24. Found: C, 78.47; H, 8.50; N, 2.48; S, 5.25.

2,5-Bis[(4-dodecyloxyphenyl)ethynyl]-4-methylthiazole (1c)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6 H *J* 6.4 Hz, CH_3), 1.26 (br s, 36 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 2.56 (s, 3 H, CH_3), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.87 (d, 4 H, *J* 8.6 Hz, ArH), 7.44 (d, 2 H, *J* 8.4 Hz, ArH), 7.50 (d, 2 H, *J*

8.4 Hz, ArH). IR (KBr) 2210 cm^{-1}. Anal. Calcd for $C_{44}H_{61}NO_2S$: C, 79.17; H, 9.14; N, 2.10; S, 4.80. Found: C, 79.34; H, 8.92; N, 2.21; S, 4.72.

2,5-Bis[(4-tetradecyloxyphenyl)ethynyl]-4-methylthiazole (1d)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6 H *J* 6.4 Hz, CH_3), 1.26 (br s, 44 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 2.56 (s, 3 H, CH_3), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.87 (d, 4 H, *J* 8.6 Hz, ArH), 7.44 (d, 2 H, *J* 8.4 Hz, ArH), 7.50 (d, 2 H, *J* 8.4 Hz, ArH). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{48}H_{69}NO_2S$: C, 79.68; H, 9.54; N, 1.93; S, 4.43. Found: C, 79.61; H, 9.48; N, 1.96; S, 4.54.

2,5-Bis[(4-hexadecyloxyphenyl)ethynyl]-4-methylthiazole (1e)

^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 0.88$ (t, 6 H *J* 6.4 Hz, CH_3), 1.26 (br s, 52 H, CH_2), 1.79 (quint, 4 H, *J* 6.8 Hz, CH_2), 2.56 (s, 3 H, CH_3), 3.98 (t, 4 H, *J* 6.4 Hz, OCH_2), 6.87 (d, 4 H, *J* 8.6 Hz, ArH), 7.44 (d, 2 H, *J* 8.4 Hz, ArH), 7.50 (d, 2 H, *J* 8.4 Hz, ArH). IR (KBr) 2200 cm^{-1}. Anal. Calcd for $C_{52}H_{77}NO_2S$: C, 80.11; H, 9.88; N, 1.80; S, 4.11. Found: C, 79.90; H, 9.78; N, 1.84; S, 3.92.

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