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## Liquid Crystals

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# Synthesis of laterally substituted bistolane liquid crystals

C. S. HSU\*, K. F. SHYU, Y. Y. CHUANG

Department of Applied Chemistry, National Chiao Tung University, Hsinchu,  
Taiwan 30050, ROC

and SHIN-TSON WU

HRL Laboratories, 3011 Malibu Canyon Road, Malibu, CA 90265, USA

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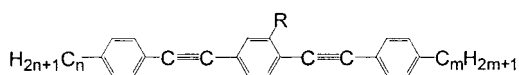
Methods for synthesizing bistolane liquid crystal materials with lateral methyl and ethyl substituents are presented. Some of the bistolanes are nematic at room temperature. These highly conjugated mesogens exhibit wide nematic ranges, small enthalpies of fusion, high birefringence and modest viscosity. Their potential applications for flat panel displays employing light scattering or Bragg reflection and for infrared optically phased arrays are foreseeable.

## 1. Introduction

High birefringence ( $\Delta n$ ) liquid crystals (LCs) are attractive for display devices involving light scattering [1] or Bragg reflection [2], and for beam steering devices employing voltage-controlled phase gratings [3, 4]. From the single band model, [5] the  $\Delta n$  of a LC is mainly determined by its molecular conjugation, differential oscillator strength and order parameter. A more linearly conjugated LC should, in principle, have a larger birefringence. A major technical challenge in high  $\Delta n$  LC studies is however to reduce melting temperatures.

Asymmetric diphenyl-diacetylene LCs possess a high birefringence, low viscosity and low melting point, [6–9] but, they are sensitive to UV radiation. Some symmetric bistolanes have been reported in the literature [10–13], but their melting points are extraordinarily high ( $> 200^\circ\text{C}$ ). Recently, we discovered that lateral alkyl substitution in the middle phenyl ring significantly lowers the melting temperatures of bistolane LCs. Some bistolanes remain liquid at room temperature and their clearing point exceeds  $100^\circ\text{C}$ . These bistolanes are chemically stable and will find useful applications.

In this paper, we report the synthesis processes and physical properties of two series of bistolane LCs containing a lateral alkyl substituent. The general bistolane structures that we have studied are:



\* Author for correspondence

Here,  $R$  is a methyl or ethyl group and  $n$  and  $m$  are limited to  $1 \sim 6$  for low viscosity consideration. The synthesis schemes are described in §2. The structure–property relationships for these compounds are discussed in §3.

## 2. Experimental

### 2.1. Characterization techniques

$^1\text{H}$  NMR spectra (30 MHz) were recorded on a Varian VXR-300 spectrometer. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory. Heating and cooling rates were  $10^\circ\text{C min}^{-1}$ . Transition temperatures reported here were collected during the second heating and cooling scans. A Carl-Zeiss Axiphot optical polarizing microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and analyse the anisotropic mixtures.

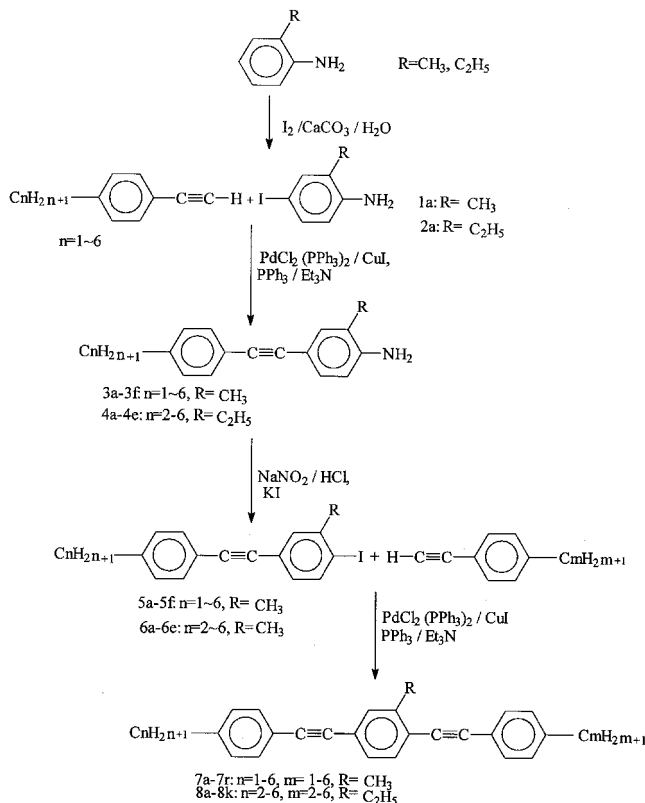
### 2.2. Synthesis of laterally substituted bistolanes

The scheme illustrates the procedures used to synthesize the laterally substituted bistolane compounds.

#### 2.2.1. Synthesis of 4-iodo-2-methylaniline (**1a**) and 4-iodo-4-ethylaniline (**2a**)

Compounds **1a** and **2a** were prepared by analogous methods. The synthesis of compound **1a** is described below.

*o*-Toluidine (20 g, 0.187 mol), iodine (47.5 g, 0.187 mol) and calcium carbonate (23.3 g, 0.233 mol) were dissolved



Scheme. Synthesis of laterally substituted bistolane compounds.

in 100 ml of water. The solution was stirred at room temperature for 1 h and heated to 65°C for 5 min. After cooling to room temperature, the solution was added to 100 ml of water and then shaken with ethyl ether. The ether extract was dried with anhydrous  $\text{MgSO}_4$  and the solvent removed in a rotary evaporator. The crude product was recrystallized from 50% aqueous ethanol to yield 36.2 g (83%) of brown crystals; m.p. = 86.0°C.

$^1\text{H NMR}$ ,  $\delta$  = 2.09 (s, 3H,  $-\text{CH}_3$ ), 3.59 (br, 2H,  $-\text{NH}_2$ ), 6.41–7.32 (m, 3 aromatic protons).

### 2.2.2. Synthesis of 4-*n*-alkyl-3'-methyl-4'-aminotolanes (3a–3f) and 4-*n*-alkyl-3'-ethyl-4'-aminotolanes (4a–4e)

4-*n*-Alkylphenylacetylenes were prepared as previously described [9]. Both **1a** and **2a** were coupled with 4-*n*-alkylphenylacetylenes to form compounds **3a–3f** and **4a–4e**. The synthesis of compound **3c** is described below.

4-Iodo-2-methyl aniline (8.38 g, 36.0 mmol), 4-*n*-propylphenylacetylene (6.48 g, 45.0 mmol), triphenylphosphine (0.7 g, 2.7 mmol), bis(triphenylphosphine) palladium chloride (0.25 g, 0.36 mmol), and cuprous iodide (0.25 g, 1.3 mmol) were dissolved in 100 ml of triethylamine. The solution was heated at reflux for 24 h, then cooled to room temperature. The solvent was removed in a rotary evaporator and the crude product was treated with

saturated ammonium chloride solution. The product was extracted into ethyl ether. The ether solution was washed with water, saturated sodium chloride solution, and dried over anhydrous  $\text{MgSO}_4$ . After the ether was removed, the crude product was purified by column chromatography (silica gel, ethylacetate/*n*-hexane = 1/4 as eluent) to yield 8.51 g (95%) of brown crystals; m.p. = 40.0°C.

$^1\text{H NMR}$ ,  $\delta$  = 0.92 (t, 3H,  $-\text{CH}_3$ ), 1.61 (m, 2H,  $-\text{CH}_2-$ ), 2.10 (s, 3H,  $\text{Ph}-\text{CH}_3$ ), 2.56 (t, 2H,  $\text{Ph}-\text{CH}_2-$ ), 3.71 (br, 2H,  $-\text{NH}_2$ ), 6.55–7.41 (m, 7 aromatic protons).

### 2.2.3. Synthesis of 4-*n*-alkyl-3'-methyl-4'-iodotolanes (5a–5f) and 4-*n*-alkyl-3'-ethyl-4'-iodotolanes (6a–6e)

Compounds **5a–5f** and **6a–6k** were prepared by the same method. The synthesis of compound **5c** is described below.

Compound **3c** (7.25 g, 29.0 mmol) was dissolved in THF (15 ml) and cooled to 0°C. A mixture of conc. HCl (16 ml) and 40 wt % aqueous sodium nitrite (17.5 ml) was added to the THF solution. The solution was stirred at 0°C for 30 min and then treated with 6M aqueous KI (50 ml). The mixture was stirred at 0°C for 3 h, treated with saturated aqueous sodium thiosulfate (50 ml) and shaken with *n*-hexane. The *n*-hexane solution was washed with water and saturated brine, and dried over anhydrous  $\text{MgSO}_4$ . After the solvent was removed, the crude product was purified by column chromatography (silica gel, *n*-hexane as eluent) to yield 6.29 g (60%) of yellowish crystals; m.p. = 50.2°C.

$^1\text{H NMR}$ ,  $\delta$  = 0.93 (t, 3H,  $-\text{CH}_3$ ), 1.63 (m, 2H,  $-\text{CH}_2-$ ), 2.40 (s, 3H,  $\text{Ph}-\text{CH}_3$ ), 2.58 (t, 2H,  $\text{Ph}-\text{CH}_2-$ ), 6.98–7.60 (m, 7 aromatic protons).

### 2.2.4. Synthesis of bistolanes with either a lateral methyl (7a–7r) or ethyl (8a–8k) substituent

Compounds **7a–7r** and **8a–8k** were prepared by Cadiot–Chodkiewicz coupling [14] of a 4-*n*-alkylphenylacetylene with compounds **5a–5f** and **6a–6e**, respectively, according to similar synthetic procedures to those given for compound **3c**. All the compounds were purified several times by column chromatography (silica gel, *n*-hexane as eluent) until their purities were higher than 98%. The elemental analysis and purity data for some representative compounds are listed in table 1.

$^1\text{H NMR}$  of compound **7a**:  $\delta$  = 1.23 (t, 3H,  $-\text{CH}_2-\text{CH}_3$ ), 2.35 (s, 3H, lateral  $\text{Ph}-\text{CH}_3$ ), 2.67 (q, 2H,  $\text{Ph}-\text{CH}_2-$ ), 7.12–7.45 (m, 11 aromatic protons).

### 2.2.5. Synthesis 4-[2-(4-ethylphenyl)-1-ethynyl]-4'-hexyltolane (9a)

Compound **9a**, without a lateral substituent, was synthesized by two step Cadiot–Chodkiewicz couplings of the 4-*n*-alkylphenylacetylene with 1-bromo-4-iodo benzene.

Table 1. Purity and elemental analysis data for some representative bistolanes.

Compound	R	n	m	Purity/%	Elemental analysis, found (calc.)/%	
					C	H
7a	CH <sub>3</sub>	1	2	99.1	93.51 (93.37)	6.49 (6.63)
7b	CH <sub>3</sub>	1	3	98.3	93.45 (93.06)	6.55 (6.94)
7f	CH <sub>3</sub>	2	1	99.0	93.63 (93.37)	6.37 (6.63)
7g	CH <sub>3</sub>	2	2	98.5	92.70 (93.06)	7.30 (6.94)
7j	CH <sub>3</sub>	3	2	99.1	92.99 (92.77)	7.01 (7.23)
7k	CH <sub>3</sub>	3	3	99.0	92.89 (92.50)	7.11 (7.50)
7o	CH <sub>3</sub>	4	2	98.3	92.33 (92.50)	7.67 (7.50)
7p	CH <sub>3</sub>	5	2	98.4	92.01 (92.26)	7.99 (7.74)
7q	CH <sub>3</sub>	6	2	99.0	92.32 (92.03)	7.68 (7.97)
8a	C <sub>2</sub> H <sub>5</sub>	2	3	98.6	92.81 (92.50)	7.19 (7.50)
8c	C <sub>2</sub> H <sub>5</sub>	3	2	99.0	92.30 (92.50)	7.70 (7.50)
8f	C <sub>2</sub> H <sub>5</sub>	4	2	99.3	92.07 (92.26)	7.93 (7.97)
8h	C <sub>2</sub> H <sub>5</sub>	5	2	98.4	92.22 (92.03)	7.78 (7.97)
8i	C <sub>2</sub> H <sub>5</sub>	6	2	99.0	92.03 (91.81)	7.97 (8.19)

### 3. Results and discussion

#### 3.1. Effect of terminal alkyl chain length

The phase transitions and corresponding enthalpy changes for compounds **7a–7r** with a lateral methyl substituent are listed in table 2. All the compounds give an enantiotropic nematic phase.

Compounds **7a–7r** possess the same mesogenic core. The only difference amongst them is the length of the terminal alkyl groups at each end. In general, this series of compounds gives very high clear temperatures ranging from 160 to 200°C. Each compound also gives a very wide temperature range nematic phase (>45°C). The phase transition temperatures are strongly affected by the lengths of the terminal alkyl groups. From table 2, we find several interesting phase transition phenomena:

- (i) On going from **7a** to **7e**, the terminal alkyl chain length on the right-hand side increases from methyl to hexyl. Figure 1 shows the plot of the phase transition temperatures versus the carbon number ( $m$ ) of the right-hand alkyl group and demonstrates that both melting and clearing temperatures decrease gradually with increasing carbon number of the terminal alkyl group. For the other two groups of compounds, i.e. **7f–7i** and **7j–7n**, the phase transition temperatures follow the same trend as that for compounds **7a–7e**.
- (ii) For the other groups of compounds that contain the same ethyl group on the right-hand side and a different alkyl group on the left, phase transition temperatures are plotted against the carbon number ( $n$ ) of the left-hand alkyl group in figure 2. This also demonstrates that both melting and clearing temperatures decrease with increasing carbon number of the terminal alkyl group.

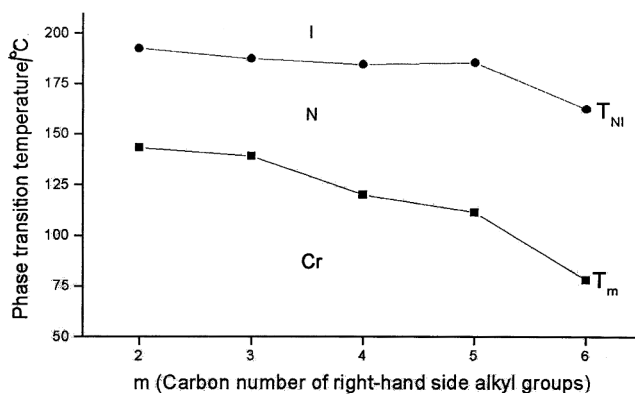


Figure 1. Melting ( $T_m$ , ■) and isotropization ( $T_{Ni}$ , ●) temperatures of the lateral methyl substituted bistolanes as a function of the carbon number ( $m$ ) of the right-hand side alkyl group.

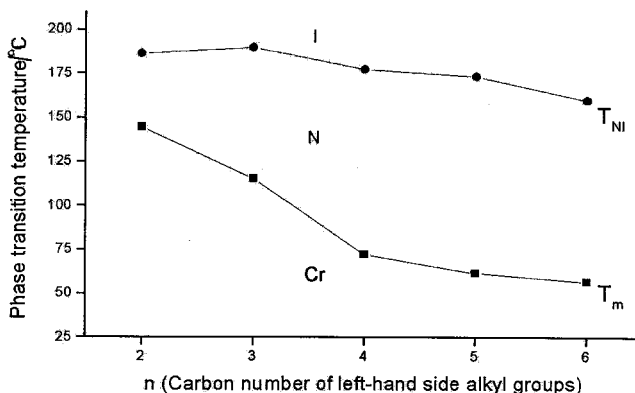


Figure 2. Melting ( $T_m$ , ■) and isotropization ( $T_{Ni}$ , ●) temperatures of the lateral methyl substituted bistolanes as a function of the carbon number ( $n$ ) of the left-hand side alkyl group.

Table 2. Phase transition temperatures and enthalpy changes for bistolanes with a lateral methyl (**7a–7r**) or ethyl (**8a–8j**) substituent and for the unsubstituted compound (**9a**).

Compound	R	n	m	T/°C (H/kJ mol)				
				Cr	N	I		
<b>7a</b>	CH <sub>3</sub>	1	2	•	143.2 (30.8)	•	192.4 (0.90)	•
<b>7b</b>	CH <sub>3</sub>	1	3	•	139.1 (27.8)	•	187.4 (0.73)	•
<b>7c</b>	CH <sub>3</sub>	1	4	•	120.2 (22.3)	•	184.6 (0.90)	•
<b>7d</b>	CH <sub>3</sub>	1	5	•	111.3 (22.5)	•	185.7 (1.05)	•
<b>7e</b>	CH <sub>3</sub>	1	6	•	78.1 (21.2)	•	162.7 (0.97)	•
<b>7f</b>	CH <sub>3</sub>	2	1	•	136.5 (29.8)	•	189.6 (0.74)	•
<b>7g</b>	CH <sub>3</sub>	2	2	•	144.5 (26.4)	•	186.4 (0.45)	•
<b>7h</b>	CH <sub>3</sub>	2	5	•	97.8 (18.9)	•	179.9 (0.97)	•
<b>7i</b>	CH <sub>3</sub>	2	6	•	73.9 (21.6)	•	166.5 (1.01)	•
<b>7j</b>	CH <sub>3</sub>	3	2	•	115.3 (22.5)	•	190.0 (1.01)	•
<b>7k</b>	CH <sub>3</sub>	3	3	•	123.4 (21.0)	•	200.4 (1.05)	•
<b>7l</b>	CH <sub>3</sub>	3	4	•	98.5 (22.0)	•	191.2 (1.40)	•
<b>7m</b>	CH <sub>3</sub>	3	5	•	86.2 (15.1)	•	182.8 (1.45)	•
<b>7n</b>	CH <sub>3</sub>	3	6	•	77.9 (15.7)	•	170.0 (1.17)	•
<b>7o</b>	CH <sub>3</sub>	4	2	•	72.2 (17.5)	•	177.4 (0.98)	•
<b>7p</b>	CH <sub>3</sub>	5	2	•	61.6 (14.8)	•	173.5 (0.94)	•
<b>7q</b>	CH <sub>3</sub>	6	2	•	56.8 (14.4)	•	160.1 (0.85)	•
<b>7r</b>	CH <sub>3</sub>	6	3	•	57.3 (13.7)	•	168.7 (1.17)	•
<b>8a</b>	C <sub>2</sub> H <sub>5</sub>	2	3	•	73.9 (14.0)	•	141.5 (0.94)	•
<b>8b</b>	C <sub>2</sub> H <sub>5</sub>	2	5	•	58.4 (11.9)	•	124.6 (1.09)	•
<b>8c</b>	C <sub>2</sub> H <sub>5</sub>	3	2	•	37.2 (13.3)	•	136.0 (0.83)	•
<b>8d</b>	C <sub>2</sub> H <sub>5</sub>	3	5	•	56.1 (12.5)	•	134.9 (1.26)	•
<b>8e</b>	C <sub>2</sub> H <sub>5</sub>	3	6	•	56.9 (12.7)	•	120.4 (1.08)	•
<b>8f</b>	C <sub>2</sub> H <sub>5</sub>	4	2	•	69.6 (27.0)	•	123.8 (0.98)	•
<b>8g</b>	C <sub>2</sub> H <sub>5</sub>	4	3	•	35.9 (18.6)	•	126.7 (1.25)	•
<b>8h</b>	C <sub>2</sub> H <sub>5</sub>	5	2	•	29.4 (13.6)	•	128.0 (1.11)	•
<b>8i</b>	C <sub>2</sub> H <sub>5</sub>	6	2	•	31.0 (13.3)	•	106.8 (0.75)	•
<b>8j</b>	C <sub>2</sub> H <sub>5</sub>	6	3	•	20.0 (14.7)	•	107.8 (1.16)	•
<b>9a</b>	H	6	2	•	133.6 (15.1)	•	191.1 (1.05)	•

- (iii) An asymmetric bistolane generally shows a much lower melting point ( $T_m$ ) than the symmetric one. For example, the  $T_m$  of compound **7k** is 123.4°C. Keeping the total carbon number of both terminal alkyl groups unchanged except for breaking the symmetry leads to a much lower  $T_m$ . For instance, the  $T_m$  of compound **7o** is reduced to 72.2°C. However, if one side has too short an alkyl chain, as in compound **7d**, then the advantage is not obvious. The  $T_m$  of compound **7d** remains as high as 111.3°C.
- (iv) Since the lateral methyl group protrudes from the 3-position of the middle phenyl ring, it is more favourable to have a longer alkyl chain on the left-hand side than on the right. This is demonstrated in the cases of the **7h/7p** and **7i/7q** pairs. The  $T_m$  values of the **7p** and **7q** homologues are 36 and 13°C lower than those of the **7h** and **7i** homologues, respectively.

### 3.2. Effect of the size of the lateral alkyl group

Table 2 summarizes also the phase transition temperatures and corresponding enthalpy changes for

compounds **8a–8j** that contain a lateral ethyl group. Compound **9a** without a lateral alkyl group in the middle phenyl ring is also included for comparison. All the compounds exhibit an enantiotropic nematic phase, and their phase transition temperatures follow the same trend as that for the previously discussed series of compounds **7a–7r**. The compounds with longer terminal alkyl chains show much lower  $T_m$  values. This series of compounds reveals much lower melting and clearing temperatures than those of the laterally methyl substituted series of compounds. This means that the size of the lateral alkyl group plays a very important role in lowering the melting point. For example, the  $T_m$  of compound **9a** is 133.6°C and the  $T_m$  of compound **7q** is 56.8°C, while the  $T_m$  of compound **8i** is as low as 31°C. This is because the lateral ethyl group increases the width of the molecule and so decreases the packing density of the LC molecules. As a result, the required temperatures to melt the crystals and to clear the LC phase are much lower.

Some homologues (e.g. compounds **8h–8j**) exhibit particularly low melting points (< 31°C) and small enthalpies

(< 15 kJ mol<sup>-1</sup>). Compound **8j** has a surprisingly low melting point. We had to cool nematic samples to -170°C and run the differential scanning calorimeter very slowly (at 1°C min<sup>-1</sup>) in order to resolve the melting point peak. In the cooling process, the solidification temperature was found to be below -50°C. This large supercooling phenomenon is very useful for formulating eutectic mixtures with a wide nematic range.

### 3.3. Physical properties

Two compounds, **7r** and **8j**, were selected for dielectric anisotropy and birefringence measurements [15, 16]. The bistolane compounds are non-polar so that the dielectric anisotropy ( $\Delta\epsilon$ ) measured was around 1. The birefringence of compound **7r** was measured by a guest-host method [17]. The refractive indices of E63 (Merck UK) and three mixtures containing E63 and 10, 20 and 30 wt % of compound **7r** were measured using a Jelly-Leitz refractometer. The extrapolated refractive indices of pure compound **7r** are:  $n_e = 1.889$ ,  $n_o = 1.507$ , or  $\Delta n = 0.382$  at a wavelength of 589 nm and  $T = 22^\circ\text{C}$ . The birefringence dispersion of compound **8j** was also measured at room temperature ( $T = 22^\circ\text{C}$ ) using a homogeneous aligned cell. The birefringence ( $\Delta n$ ) of **8j** exceeds 0.4 in the blue and green regions. As the wavelength increases,  $\Delta n$  decreases gradually and saturates in the near infrared region.

### 4. Conclusion

Two series of laterally substituted bistolane LCs were synthesized and characterized. All the bistolanes display enantiotropic nematic phases. The terminal alkyl groups have a profound effect on the phase transition temperature of the bistolanes; both melting and clearing temperatures decrease as the alkyl chain length increases. The lateral methyl or ethyl group plays an important role in lowering the melting temperature. Some homologues possess a high birefringence, low melting points and high clearing temperatures, and small enthalpies of fusion. These bistolane LCs could find useful applications

in polymer dispersed LC displays, reflective displays employing cholesteric liquid crystals and laser beam steering employing liquid crystal optically phased arrays.

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