

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Synthesis of novel nematic liquid crystals containing 3,3'-dimethyl-2,2'-bipyridyl

Chi-Han Lee; Takakazu Yamamoto

Online publication date: 11 November 2010

**To cite this Article** Lee, Chi-Han and Yamamoto, Takakazu(2002) 'Synthesis of novel nematic liquid crystals containing 3,3'-dimethyl-2,2'-bipyridyl', *Liquid Crystals*, 29: 1, 67 – 70

**To link to this Article:** DOI: 10.1080/02678290110086505

**URL:** <http://dx.doi.org/10.1080/02678290110086505>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Synthesis of novel nematic liquid crystals containing 3,3'-dimethyl-2,2'-bipyridyl

CHI-HAN LEE and TAKAKAZU YAMAMOTO\*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

(Received 1 April 2001; in final form 11 June 2001; accepted 27 June 2001)

Liquid-crystalline 3,3'-dimethyl-2,2'-bipyridyl derivatives with long 4-(alkoxyphenyl)ethynyl ( $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{OR}$ ) groups in the 5,5'-positions were synthesized by palladium-catalysed crosscoupling reactions. The compounds exhibit exclusively nematic behaviour; for example, the hexyl derivative showed a nematic phase over the temperature range 145.2–205.0°C. On increasing the length of the terminal chain, the transition temperatures were lowered; for example, the hexadecyl derivative was nematic in the range 117.0–126.8°C.

## 1. Introduction

Recently, much attention has been focused on the synthesis and properties of molecules containing the 2,2'-bipyridyl unit [1–3], since such materials are useful for applications in several fields. Liquid crystalline materials containing 2,2'-bipyridyl include thermotropic liquid crystalline polyesters incorporating 5,5'-substituted 2,2'-bipyridyl units [4] and alkanoyl derivatives of 6,6'-diamino-2,2'-bipyridyl and their metal complexes [5]. Recently, the synthesis and liquid crystalline behaviour of a homologous series of asymmetrically substituted 2,2'-bipyridyls was reported [6]. However, liquid crystals having a 3,3'-dimethyl-2,2'-bipyridyl unit have not been reported, despite the known mesogenic behaviour of other 2,2'-bipyridyl units [7].

We have found that the 3,3'-dimethyl-2,2'-bipyridyl unit serves as a useful mesogenic moiety, and report here the synthesis and nematic properties of the 5,5'-bis-[(4-*n*-alkoxyphenyl)ethynyl]-3,3'-dimethyl-2,2'-bipyridyls, **1** (figure 1).

## 2. Results and discussion

### 2.1. Synthesis

The conjugated phenylethynyl backbone is a rigid rod that can act as a mesogenic unit, and in consequence the synthesized 3,3'-dimethyl-2,2'-bipyridyl derivatives containing long alkoxy chains are liquid crystalline materials.

Compounds **1** were synthesized by palladium-catalysed cross-coupling reactions which have been reported elsewhere [8–10]; here, we focus on the crosscoupling

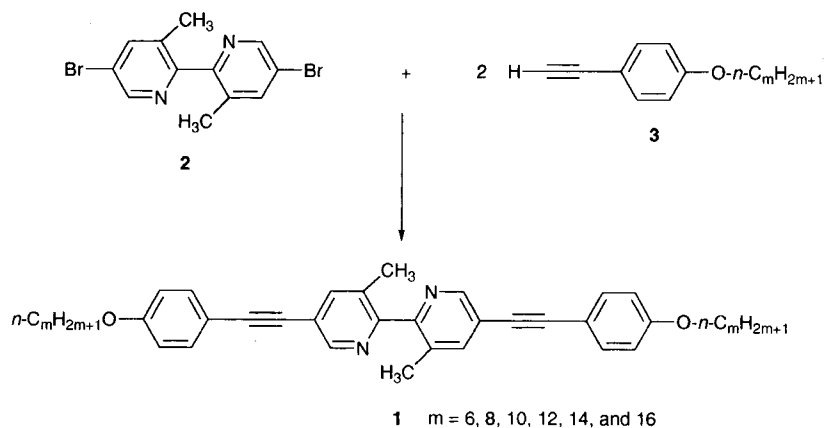
reactions of terminal alkynes having long alkoxy groups with 5,5'-dibromo-3,3'-dimethyl-2,2'-bipyridyl (**2**) [2*a*] (figure 2). Terminal phenylalkynes (**3**) having long alkoxy groups were prepared in three steps from 4-hydroxyacetophenone, as previously reported [11].

### 2.2. Thermal properties of 3,3'-dimethyl-2,2'-bipyridyl derivatives (**1a–f**)

All the 3,3'-dimethyl-2,2'-bipyridyl-based compounds **1a–f** showed mesogenic properties which were investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The heating and cooling rates were 5°C min<sup>-1</sup>. DSC thermograms of the compounds **1a–f** were measured on heating and subsequent cooling; phase transition temperatures are summarized in the table.

All the compounds **1a–f** show enantiotropic behaviour and specifically a nematic phase over a wide temperature range. This enantiotropic behaviour was confirmed by POM. As shown in the table, **1a–f** exhibit nematic phases at moderate temperatures. The synthesis of 5,5'-[(4-hexadecyloxyphenyl)ethynyl]-2,2'-bipyridyl was reported previously [9]; this compound exhibited several smectic phases (SmC, SmF and SmI) and high transition temperatures. The preparation and liquid crystal properties of 5-methyl-5'-(4-*n*-alkoxyphenylvinyl)-2,2'-bipyridyls have also been reported [4]; these compounds displayed smectic phases (SmA, SmB) and nematic phases. In contrast, the 3,3'-dimethyl-2,2'-bipyridyl-based compounds, **1a–f**, exhibit only nematic behaviour under POM. The texture observed for all the compounds **1a–f** is a characteristic schlieren texture. It has also recently been reported that some polyamides based on the 2,2'-bipyridyl unit form lyotropic mesophases [12].

\* Author for correspondence  
e-mail: tyamamot@res.titech.ac.jp

Figure 1. Structure of the 5,5'-bis[(4-*n*-alkoxyphenyl)ethynyl]-3,3'-dimethyl-2,2'-bipyridyl series, **1**.Figure 2. Synthetic route to **1**: for conditions see text.Table. Phase transition temperatures of compounds **1**: Cr, crystal; N, nematic; I, isotropic.

Compound	<i>m</i>	Phase transition temperature/°C	
<b>1a</b>	6	Cr $\xrightleftharpoons[127.3]{145.2}$ N	N $\xrightleftharpoons[187.8]{205.0}$ I
		<b>1b</b>	8
<b>1c</b>	10		
		<b>1d</b>	12
<b>1e</b>	14		
		<b>1f</b>	16

Compounds **1a** and **1b** show a wide liquid crystalline temperature ranges and their transition temperatures are higher than those of the compounds, **1c–f**. In particular, compound **1a** exhibits a high nematic–isotropic transition temperature (205.0°C). This presumably reflects its greater structural anisotropy compared with the other compounds, **1b–f**. The significance of the extensive supercooling of the nematic phase, however, is unclear, see the table. The data shown in the table are reproducible, and the compounds do not undergo thermal degradation in the temperature ranges studied. The lowering of the transition temperatures on increasing in the length of the alkyl chain can be explained by the increase in the fraction of mobile components which perturb the molecular

cooperative packing by decreasing the segregation between aromatic and aliphatic fragments [13]. This effect has been also observed in polycatenar compounds [14].

On heating from room temperature, the DSC trace shows two sharp endothermic peaks indicative of first order transitions, as shown in figure 3 for **1f**. The lower temperature strong peak clearly corresponds to a transition involving strong disordering of a highly ordered crystal phase. The higher temperature peak is assigned to the transition from the liquid crystalline phase to an isotropic liquid phase. It is clear that the transition from the crystal to the liquid crystalline phase has a much higher associated enthalpy change than the transition from the liquid crystal to the isotropic phase. On cooling from the melt, the thermogram shows two sharp exothermic peaks. These thermal data are summarized in the table.

### 3. Conclusions

A new class of 3,3'-dimethyl-2,2'-bipyridyl derivatives, **1a–f**, having long alkoxy groups has been synthesized and their thermal properties and the effects of the alkoxy chain length have been investigated. These compounds were thermotropic liquid crystalline materials and exhibit only nematic behaviour.

### 4. Experimental

#### 4.1. Synthesis

##### 4.1.1. 3,3'-Dimethyl-2,2'-dibromobipyridyl (**2**)

A literature method was used for the synthesis of this compound [2a].

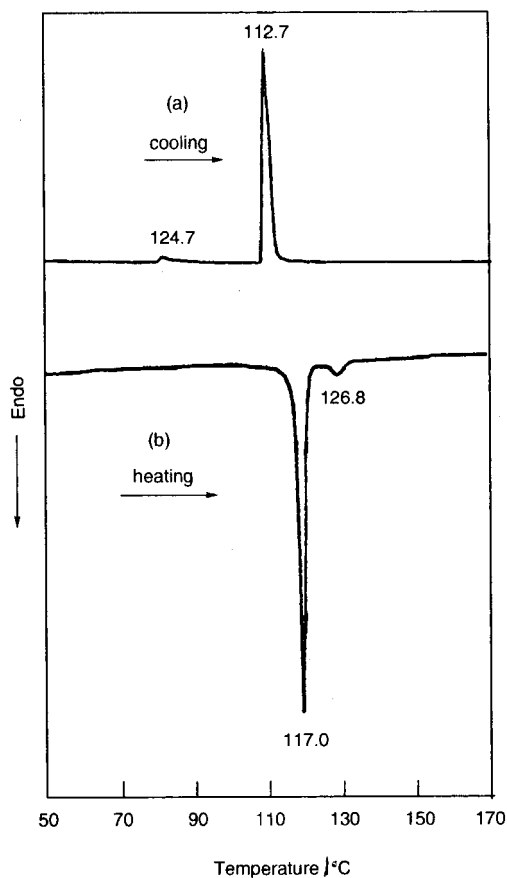


Figure 3. DSC traces observed on (a) heating and (b) cooling compound **1f**: heating and cooling rates of  $5^{\circ}\text{C min}^{-1}$  under nitrogen were employed.

#### 4.1.2. 4-Alkoxyphenylacetylene s (**3**)

These were prepared as previously reported [11].

#### 4.1.3. Synthesis of 5,5'-Bis[(4-alkoxyphenyl)ethynyl]-3,3'-dimethyl-2,2'-bipyridyl (**1a-f**)

A mixture of 3,3'-dimethyl-2,2'-dibromobipyridyl (68.4 mg, 0.2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (23.1 mg, 0.02 mmol),  $\text{CuI}$  (3.8 mg, 0.02 mmol), and appropriate 4-alkoxyphenylacetylene (0.42 mmol), freshly distilled triethylamine (1 ml) and anhydrous THF (10 ml) was degassed and stirred at r.t. for 20 h under argon. After the mixture was concentrated by evaporation, the residue was washed with saturated aqueous  $\text{NH}_4\text{Cl}$  and extracted with chloroform ( $3 \times 20$  ml). The combined extracts were washed with water and brine, and then dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent removed. The product was purified by column chromatography ( $\text{SiO}_2$ , ethyl acetate) and recrystallization from methanol/hexane to yield compounds **1a-f** in 88–90% yield. The following analytical data for **1a** are typical for all members of this series of compounds.

Elemental analysis:  $\text{C}_{40}\text{H}_{44}\text{N}_2\text{O}_2$  ( $M_w = 584.8$ ); calc C 82.15, H 7.52, N 4.79; found, C 81.93, H 7.41, N 4.76%. IR (KBr):  $\nu = 2210$  ( $\text{C}\equiv\text{C}$ )  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta = 0.90$  (t, 6H,  $J = 6.4$  Hz,  $\text{CH}_3$ ), 1.32 (br, 12H,  $\text{CH}_2$ ), 1.80 (quint, 4H,  $J = 6.4$  Hz,  $\text{CH}_2$ ), 2.19 (s, 6H,  $\text{CH}_3$ ), 3.98 (t, 4H,  $J = 6.4$  Hz,  $\text{OCH}_2$ ), 6.89 (d, 4H,  $J = 8.8$  Hz, ArH), 7.49 (d, 4H,  $J = 8.8$  Hz, ArH), 7.75 (s, 2H, Py), 8.65 (s, 2H, Py) ppm.

#### 4.2. Characterization

$^1\text{H}$  NMR spectra were obtained using a Jeol JNM-LA 300 (300 MHz) NMR spectrometer. 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 using a polarizing microscope (Olympus, BHSP) equipped with a Mettler hot stage TH-600RH and a controller (Japan Hytech, TH-600RH) and also on the basis of the thermograms recorded using a differential scanning calorimeter (Rigaku, Thermoflex, DSC 8230).

The authors acknowledge Mr Y. Sano for his assistance with DSC and Professor M. Matsumoto of Kyushu Sangyo University for helpful discussions. Financial support for this work was provided by the Japan Society for the Promotion of Science.

#### References

- [1] EAVES, J. G., MUNRO, M. S., and PARKER, D., 1985, *J. chem. Soc., chem. Commun.*, 684.
- [2] (a) YAMAMOTO, T., MARUYAMA, T., ZHOU, Z.-H., ITO, T., FUKUDA, T., YONADA, Y., BEGUM, F., IKEDA, T., SASAKI, S., TAKEZOE, H., FUKUDA, A., and KUBOTA, K., 1994, *J. Am. chem. Soc.*, **116**, 4832; (b) SATO, Y., KAGOTANI, M., YAMAMOTO, T., and SOUMA, Y., 1999, *Appl. Catal. A: Gen.*, **185**, 219.
- [3] (a) LEY, K. D., LI, Y., JOHNSON, J. V., POWELL, D. H., and SCHANGE, K. S., 1999, *Chem. Commun.*, 1749; (b) ZHU, S. S., and SWAGER, T. M., 1997, *J. Am. chem. Soc.*, **119**, 12 568; (c) LEY, K. D., WHITTLE, C. E., BARTHERGER, M. D., and SHANGE, K. S., 1997, *J. Am. chem. Soc.*, **119**, 3423; (d) WANG, B., and WASIELEWSKI, M. R., 1997, *J. Am. chem. Soc.*, **119**, 12.
- [4] HANABUSA, K., HIGASHI, J.-I., KOYAMA, T., SHIRAI, H., HOJO, N., and KUROSE, A., 1989, *Makromol. Chem.*, **190**, 1.
- [5] KUBOKI, T., ARAKI, K., YAMADA, M., and SHIRISHI, S., 1994, *Bull. chem. Soc. Jpn.*, **67**, 948.
- [6] (a) DOUCE, L., ZIESSEL, R., SEGHRUCHNI, R., SKOULIOS, A., CAMPILLOS, E., and DESCHENAUX, R., 1995, *Liq. Cryst.*, **18**, 157; (b) DOUCE, L., ZIESSEL, R., SEGHRUCHNI, R., SKOULIOS, A., CAMPILLOS, E., and DESCHENAUX, R., 1996, *Liq. Cryst.*, **20**, 235.

- [7] SERRANO, L. J. (editor), 1995, *Metallomesogens* (Weinheim: Wiley-VCH).
- [8] (a) DIECK, H. A., and HECK, R. F., 1975, *J. organomet. Chem.*, **93**, 259; (b) SONOGASHIRA, K., TOHADA, Y., and HAGIHARA, N., 1975, *Tetrahedron Lett.*, 4467; (c) DAVIS, S. G., 1982, *Organotransition Metal Chemistry: Syntheses* (Oxford: Pergamon); (d) TAKAHASHI, S., KUROYAMA, Y., SONOGASHIRA, K., and HAGIHARA, N., 1980, *Synthesis*, 627.
- [9] (a) HECK, R. F., 1990, *Palladium Reagents in Organic Syntheses* (New York: Academic Press); (b) HARTLEY, F. A., 1973, *The Chemistry of Platinum and Palladium* (London: Applied Science Publishers), p. 327.
- [10] OSAKADA, K., SAKATA, R., and YAMAMOTO, T., 1997, *J. chem. Soc., Dalton Trans.*, 1265.
- [11] (a) KITAMURA, T., LEE, C. H., TANIGUCHI, Y., FUJIWARA, Y., MATSUMOTO, M., and SANO, Y., 1997, *J. Am. chem. Soc.*, **119**, 619; (b) KITAMURA, T., LEE, C. H., TANIGUCHI, H., MATSUMOTO, M., and SANO, Y., 1994, *J. org. Chem.*, **59**, 8053.
- [12] YU, S. C., HON, S., and CHAN, W. K., 2000, *Macromolecules*, **33**, 3259.
- [13] LEBLANC, K., BERDAGUE, P., RAUIT, J., BAYLE, J.-P., and JUDEINSTEIN, P., 2000, *Chem. Commun.*, 1291.
- [14] NGUYEN, H. T., DESTRADE, C., and MALTHETE, J., 1997, *Adv. Mater.*, **9**, 375.