

Title	Chiral nitroxide radical with terminal trifluoromethoxy group
Author(s)	Uchida, Yoshiaki; Akita, Takuya; Nishiyama, Norikazu
Citation	Liquid Crystals. 2023, 50(7-10), p. 1292-1295
Version Type	AM
URL	https://hdl.handle.net/11094/98294
rights	© 2023 Informa UK Limited, trading as Taylor & Francis Group.
Note	

Osaka University Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

Osaka University

Chiral Nitroxide Radical with Terminal Trifluoromethoxy Group

Yoshiaki Uchida, Takuya Akita, Norikazu Nishiyama

Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

e-mail: y.uchida.es@osaka-u.ac.jp

Chiral Nitroxide Radical with Terminal Trifluoromethoxy Group

A new chiral liquid crystalline nitroxide radical with a terminal trifluoromethoxy group exhibits not only chiral nematic and chiral smectic A phases but also a twist grain boundary phase in the cooling process. The layer order induced by the trifluoromethoxy group seems frustrated with the helical order.

Keywords: nitroxide radical; frustration; chirality; terminal group

Introduction

Liquid crystalline (LC) compounds incorporating a chiral nitroxide group into their mesogen cores (LC-NRs) show unique magnetic properties [1][2]. The core nitroxide group gives the molecule chirality, large electric dipole moments, and paramagnetic properties. They affect the phase transition behaviour of the compound; large electric dipole moments decide intermolecular attraction and repulsion [3], and chirality in the mesogen core strongly induces twisted structures [4]. There have been LC-NRs showing a variety of LC phases; nematic [5], chiral nematic [5], smectic A [6], chiral smectic A [6], smectic C [6], chiral smectic C [7], twist grain boundary [6] and columnar phases [8].

Several LC-NRs have a terminal group with a large electric dipole moment along with the molecular long axis: hydroxy [8], cyano [9], formyl [10], iodo [11] and fluoro [12] and trifluoromethoxy groups [13]. In particular, a racemate of an LC-NR with a trifluoromethoxy group shows a cybotactic nematic phase [13]; its terminal trifluoromethoxy group induces a local layer structure in the nematic phase. We expect that the enantiomerically pure sample of the same compound gives some frustration behaviors based on the terminal trifluoromethoxy group inducing cybotactic clusters of the racemate. Here, we report the phase transition behaviour of the LC-NR with a trifluoromethoxy group, as shown in Figure 1.

Experimental

Enantiomeric excess (*ee*) was determined by HPLC analysis using a chiral stationary phase column (Daicel Chiralcel OD-H, 0.46 × 25 cm). Phase transition temperatures were determined by differential scanning calorimetry (SHIMADZU DSC-60), X-ray diffraction measurements, and polarized optical microscopy (Olympus BX51). A hot stage (Japan High Tech 10083) was used as the temperature control unit for microscopy. The data were collected using a Rigaku RINT2200/PC-LH diffractometer using Cu-K α radiation with 0.15418 nm for variable temperature X-ray diffraction measurements.

Results and discussion

First, we measured the enantiomeric excess (*ee*) of **1** using high-performance liquid chromatography and confirmed that it is the *2R,5R* enantiomer with 100% *ee*, as shown in Figure 2. The phase transition behaviours of **1** are characterised by differential scanning calorimetry (DSC) analysis at a scanning rate of 2 °C min⁻¹ upon heating and cooling processes, as shown in Figure 3, and polarised optical microscopy (POM), as shown in Figure 4. During the heating run, compound **1** showed a stable chiral nematic phase from 75.2°C to 85.8°C. The POM image shows an oily streak texture typical of N* phases, as shown in Figure 4a. The POM image shows a blurred fan-shaped texture typical of twist grain boundary (TGB) phases on the transition from the N* phase at 60.0°C in the cooling run, as shown in Figure 4b [14]. We observed a fan-shaped texture typical of chiral smectic A (SmA*) phases after the transition, as shown in Figure 4c. We hypothesized that compound **1** displays an enantiotropic N* phase and monotropic TGB and SmA* phases.

X-ray diffraction (XRD) measurement further characterizes these phase transitions. The XRD measurements of compound **1** were carried out in the temperature

range of 70–100°C in the heating process and 100–50°C in the cooling process. No peak was observed in the N* phase during the heating process and between 100.0°C and 60.0°C during the cooling process (Figure 5a). Meanwhile, diffuse small-angle scattering appeared around $2\theta = 3.21^\circ$ at 56.0°C. The *d*-spacing is about 2.8 nm. Comparing it with the previously reported molecular length (3.8 nm) estimated from the density functional theory [13], we guess that interdigitated layers constitute the SmA phase. The trifluoromethoxy group seems to induce frustration between the layer and helical orders.

Conclusions

We synthesised enantiomerically pure LC-NRs with a terminal trifluoromethoxy group. The new LC-NR exhibits not only N* and SmA* phases but also a TGB phase in the cooling process. We can conclude that the layer order induced by the trifluoromethoxy group is frustrated with the helical order to give the TGB phase. The new compound help to elucidate the origin of various liquid crystal phases based on microscopic components as one of the spin-labelled LC molecules like various LC radicals [15-19].

Acknowledgements

The authors thank Professor Rui Tamura, Kyoto University, for experimental support, including X-ray diffraction measurements. This work was supported in part by the Japan Science and Technology Agency (JST) “Precursory Research for Embryonic Science and Technology (PRESTO)” for a project on “Molecular technology and creation of new function” and by the Japan Society for the Promotion of Science (JSPS) KAKENHI (Grant numbers JP17H04896 and JP20K21226). T. A. is grateful to the JSPS Research Fellowships for Young Scientists JP16J05585. We appreciate Mr. S. Nakagami, Mr. K. Hanada and Mr. Y. Inukai for their experimental support.

References

- [1] Uchida Y, Ikuma N, Tamura R, Shimono S, Noda Y, Yamauchi J, Aoki Y, Nohira H. Unusual intermolecular magnetic interaction observed in an all-organic radical liquid crystal. *J Mater Chem*. 2008;18(25):2950–2952.
- [2] Uchida Y, Suzuki K, Tamura R, Ikuma N, Shimono S, Noda Y, Yamauchi J. Anisotropic and Inhomogeneous Magnetic Interactions Observed in All-Organic Nitroxide Radical Liquid Crystals. *J Am Chem Soc*. 2010;132(28):9746–9752.
- [3] Maier W, Saupe A. Eine einfache molekular-statistische Theorie der nematischen kristallinflüssigen Phase. Teil II. *Naturforsch*. 1960;15a II(4):287–292.
- [4] de Gennes PG, Prost J. *The Physics of Liquid Crystals*. New York (NY): Oxford University Press; 1993.
- [5] Ikuma N, Tamura R, Shimono S, Kawame N, Tamada O, Sakai N, Yamauchi J, Yamamoto Y. Magnetic Properties of All-Organic Liquid Crystals Containing a Chiral Five-Membered Cyclic Nitroxide Unit within the Rigid Core. *Angew Chem Int Ed*. 2004;43(28):3677–3682.
- [6] Uchida Y, Tamura R, Ikuma N, Yamauchi J, Aoki Y, Nohira H. Synthesis and Characterization of Novel Radical Liquid Crystals Showing Ferroelectricity. *Ferroelectrics*. 2008;365(1):158–169.
- [7] Ikuma N, Tamura R, Shimono S, Uchida Y, Masaki K, Yamauchi J, Aoki Y, Nohira H. Ferroelectric Properties of Paramagnetic, All-Organic, Chiral Nitroxyl Radical Liquid Crystals. *Adv Mater*. 2006;18(4):477–480.
- [8] Nakagami S, Akita T, Kiyohara D, Uchida Y, Tamura R, Nishiyama N. Molecular Mobility Effect on Magnetic Interactions in All-Organic Paramagnetic Liquid Crystal with Nitroxide Radical as a Hydrogen-Bonding Acceptor. *J Phys Chem B*. 2018;122(29):7409–7415.
- [9] Akita T, Kiyohara D, Yamazaki T, Uchida Y, Nishiyama N. Large negative magneto-LC effects induced by racemic dimerization of liquid crystalline nitroxide radicals with a terminal cyano group. *J Mater Chem C*. 2017;5(47):12457–12465.
- [10] Suzuki K, Uchida Y, Tamura R, Shimono S, Yamauchi J. Observation of positive and negative magneto-LC effects in all-organic nitroxide radical liquid crystals by EPR spectroscopy. *J Mater Chem*. 2012;22(14):6799–6806.

- [11] Akita T, Yamazaki T, Uchida Y, Nishiyama N. Magnetic properties of terminal iodinated nitroxide radical liquid crystals. *Polyhedron*. 2017;136:79–86.
- [12] Akita T, Uchida Y, Nishiyama N. Terminal Fluorinated Nitroxide Radical Liquid Crystalline Compounds. *Mol Cryst Liq Cryst*. 2015;613(1):174–180.
- [13] Uchida Y, Akita T, Hanada K, Kiyohara D, Nishiyama N. Molecular clustering behaviour in the cybotactic nematic phase of a spin-labelled liquid crystal. *J Mater Chem C*. 2022;10(17):6621–6627.
- [14] Dierking I. *Textures of Liquid Crystals*. Revised ed. Weinheim (DE): Wiley-VCH; 2003.
- [15] Stewart D, Imrie CT. Synthesis and characterization of spin-labelled and spin-probed side-chain liquid crystal polymers. *Polymer*. 1996;37(15):3419–3425.
- [16] Ravat P, Marszalek T, Pisula W, Müllen K, Baumgarten M. Positive Magneto-LC Effect in Conjugated Spin-Bearing Hexabenzocoronene. *J Am Chem Soc*. 2014;136(37):12860–12863.
- [17] Bajzíkova K, Kohout M, Tarábek J, Svoboda J, Novotná V, Vejpravová J, Pocięcha D, Gorecka E. All-organic liquid crystalline radicals with a spin unit in the outer position of a bent-core system. *J Mater Chem C*. 2016;4(48):11540–11547.
- [18] Jasiński M, Szczytko J, Pocięcha D, Monobe H, Kaszyński P. Substituent-Dependent Magnetic Behavior of Discotic Benzo[e][1,2,4]triazinyls. *J Am Chem Soc*. 2016;138(30):9421–9424.
- [19] Castellano S, López-Calahorra F, Brillas E, Juliá L, Velasco D. All-Organic Discotic Radical with a Spin-Carrying Rigid-Core Showing Intracolumnar Interactions and Multifunctional Properties. *Angew Chem Int Ed*. 2009;48(35):6516–6519.

Figure 1. Molecular structure of **1**. The phase transition temperatures shown here are measured in the first heating process from the crystalline phase and the first cooling process from the isotropic phase. For reference, the phase transition behavior of the racemate is also described [13].

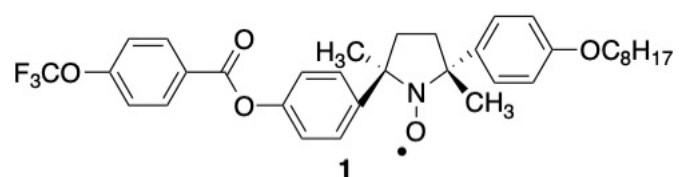
Figure 2. Determination of the *ee* value of **1** by HPLC analysis using Daicel Chiralcel OD-H (0.46 cm × 25 cm) and a mixture of hexane and 2-propanol as the mobile phase (1.0 mL h⁻¹) at 40°C; (a) 2*R*,5*R* enriched sample of 100% *ee* and (b) racemic sample. The unit for the horizontal axis is minutes.

Figure 3. DSC analysis for **1** in the first heating and cooling processes (2°C min⁻¹).

Figure 4. Polarizing optical micrographs of **1**. (a) An oily streak texture at 75.0°C in the cooling process. (b) A blurred fan-shaped texture at 60.0°C in the cooling process. (c) A fan-shaped texture at 60.0°C in the cooling process.

Figure 5. X-ray diffraction patterns of **1**. (a) 68.0°C in the cooling process. (b) 56.0°C in the cooling process.

Figure 1.



Heating: Cr 75.2 N* 85.8 Iso
Cooling: Cr < 30 SmA* 60.0 TGB 60.0 N* 85.1 Iso

cf. rac-1
Heating: Cr 77.4 N 86.4 Iso
Cooling: Cr < 30 SmA 65.3 N 84.9 Iso

Figure 2.

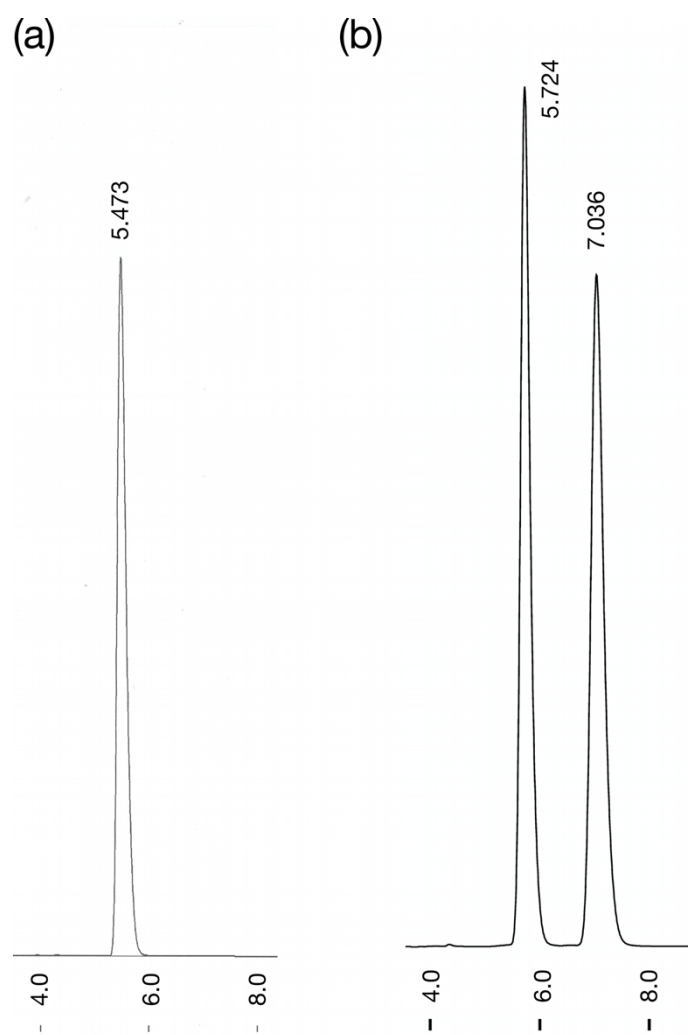


Figure 3.

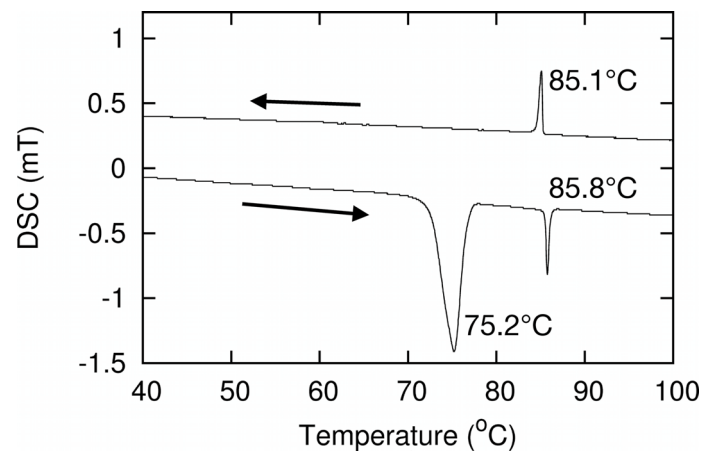


Figure 4.

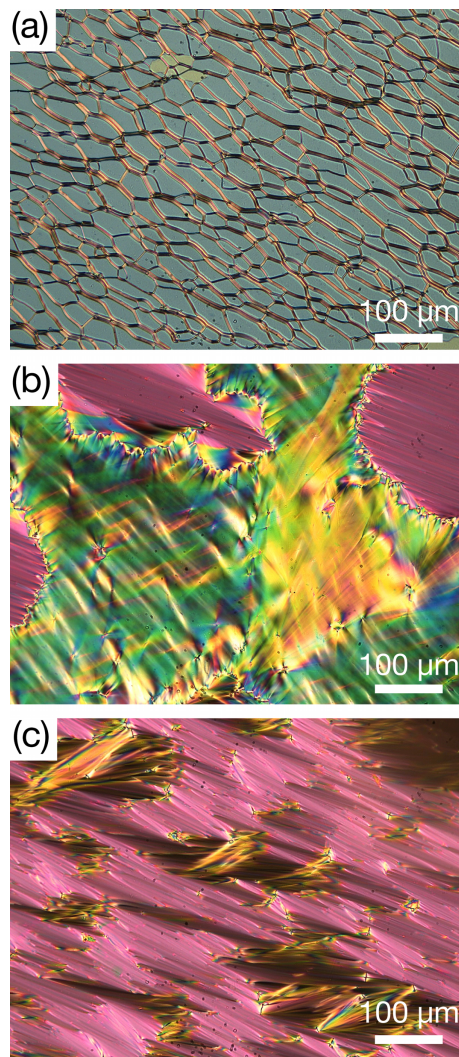


Figure 5.

