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Author(s)	Uchida, Yoshiaki; Akita, Takuya; Nishiyama, Norikazu
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# 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-Ka 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 2*R*,5*R* 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<sup>-1</sup> 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].

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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  $\times$  25 cm) and a mixture of hexane and 2-propanol as the mobile phase (1.0 mL h<sup>-1</sup>) 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<sup>-1</sup>).

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.