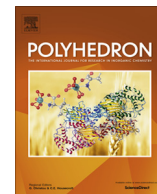




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# Magnetic properties of terminal iodinated nitroxide radical liquid crystals

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## ABSTRACT

We designed and synthesized terminal iodinated nitroxide radical liquid crystalline compounds (NR-LCs) with octyloxy side chain ( $\pm$ )-**8-I** and dodecyloxy side chain ( $\pm$ )-**12-I** to understand the substitution effects of an iodine atom on the phase transition behavior and on the magnetic properties in crystalline (Cr), liquid crystalline (LC) and isotropic (Iso) phases. These NR-LCs show monotropic nematic phases because the iodine atom is too short and apolar as a terminal group to stabilize LC phases. Furthermore, the SQUID magnetometry and electron paramagnetic resonance (EPR) spectroscopy indicate that the magnetic properties in the Cr phase depend on the length of the alkoxy side chain; antiferromagnetic interactions occur in ( $\pm$ )-**8-I**, whereas ferromagnetic interactions occur in ( $\pm$ )-**12-I**, and the paramagnetic susceptibility of ( $\pm$ )-**8-I** slightly decreases ( $\bar{j} < 0$ ) and that of ( $\pm$ )-**12-I** abruptly increases ( $\bar{j} > 0$ ) at each of the Cr-to-Iso phase transitions. These results suggest that the most frequent type of the magnetic interactions in LC and Iso phases is similar to those in the Cr phases among the various types of intermolecular magnetic interactions induced by the inhomogeneous intermolecular contacts.

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## 1. Introduction

Recently, all-organic paramagnetic rod-like liquid crystalline compounds containing a five-membered ring nitroxide radical (NR) moiety in the molecular core (NR-LCs) have attracted a great deal of attention because of their fascinating properties in externally applied fields. For example, some of them show liquid crystalline (LC) phases such as nematic (N), chiral N ( $N^*$ ), smectic A (SmA), chiral SmA (SmA\*), smectic C (SmC) and chiral SmC (SmC\*) phases [1–3], and their molecular reorientation occurs in uniform magnetic and electric fields [4–6]. Furthermore, their magnetic properties can be changed by the electric-field-induced molecular reorientation in their SmC\* phase [5]. In addition, NR droplets are attracted by a magnet [7], and spin glass-like inhomogeneous ferromagnetic interactions (Magneto-LC effects) occur in the LC phases of rod-like NR compounds [8]; the magneto-LC effects lead to an abrupt increase of paramagnetic susceptibility at crystalline (Cr)-to-LC or Cr-to-isotropic (Iso) phase transitions (positive magneto-LC effects,  $\bar{j} > 0$ ). In contrast, some of the rod-like NR compounds show averagely weak antiferromagnetic interactions (negative magneto-LC effects,  $\bar{j} < 0$ ) [3].

One of the factors to decide the sign and magnitude of the magneto-LC effects is the direction and distance between each pair of molecules contacting with each other in LC or Iso phases [8]. The manner of the intermolecular contacts depends both on phases and on molecular structures. In fact, the modification of a mesogen core and side chains, which are typical components of calamitic LC compounds, is effective to tune the phase transition behavior; e.g., longer side chains induce a highly-ordered smectic (Sm) phases than N or  $N^*$  phases [3]. Moreover, in some cases, a hydrogen-bonded mesogen core can stabilize the LC phases of NR-LCs [9] because the hydrogen-bonded core plays the same role as the covalent-bonded one [10]. Furthermore, since the introduction of the hydrogen-bonding generally decreases the orientational order parameter of the LC phases [11,12], the inhomogeneity increases and magneto-LC effects become twice as strong as those of the corresponding covalent-bonded analogue [9]. Furthermore, the molecular chirality also considerably influences the sign and magnitude of the magneto-LC effects; even if the racemic sample of a chiral NR compound shows the negative effects, the enantiomerically enriched sample of the same compound shows the positive effects [3]. To enhance the magneto-LC effects by the precise design of molecular structures, more detailed understanding of the origin of the magneto-LC effects is needed.

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In this paper, we focus on the correlation between the magnetic interactions in Cr phases and those in LC or Iso phases. In a Cr phase of an ordinary organic monoradical, there are only one or two types of intermolecular magnetic interactions. In contrast, in a fluid phase of the same compound, there should be countless types of the magnetic interactions. However, there could be only intermolecular magnetic interactions similar to those of the Cr phases in some fluid phases. To obtain such compounds, we have designed and synthesized compounds ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I** with a terminal iodine atom, whose bulkiness and ability to form the halogen-bonding could induce the similarity of the molecular packing manners in LC and Cr phases. Here, we report the synthesis of ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I** and discuss the phase transition behaviors and the magneto-LC effects in the LC and Iso phases by means of SQUID magnetometry and electron paramagnetic resonance (EPR) spectroscopy, which has proved to be an excellent tool to analyze the magnetic interactions operating in the LC and Iso phases of rod-like NR compounds around ambient temperature [8].

## 2. Materials and methods

Mass spectra were recorded on a JEOL JMS-700. IR spectra were recorded with a SHIMADZU IRAffinity-1. Elemental analyses (CHN) were obtained on a PerkinElmer 2400II. EPR spectra were recorded with a JEOL JES-FE1XG. Magnetizations were recorded with a QUANTUN DESIGN MPMS-3. Phase transition behaviors were determined by differential scanning calorimetry (DSC) (SHIMADZU DSC-60), polarized optical microscopy (Olympus BX51) and X-ray diffraction (XRD) measurement. A hot stage (Japan High Tech, 10083) was used as the temperature control unit for the microscopy. For variable temperature XRD measurement, the data collections were performed on a Rigaku RINT2200/PC-LH diffractometer using Cu-K $\alpha$  radiation with 1.5418 Å. Unless otherwise noted, solvents and reagents were reagent grade and used without further purification. X-ray crystal structure was analyzed using a Rigaku Osmic Var-iMax diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71075$  Å). Tetrahydrofuran (THF) that was used for electron paramagnetic resonance (EPR) spectroscopy was distilled from sodium/benzophenone ketyl under nitrogen.

### 2.1. Synthesis of ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I**

Racemates of phenolic NR compounds were prepared as a precursor according to the previously reported procedure [13]. The phenolic NR compounds were esterified with 4-iodobenzoic acid to afford ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I** as shown in Scheme 1. Dichloromethane (50 mL) was charged with the phenolic NR compound (0.30 mmol), 4-iodobenzoic acid (0.33 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC.HCl, 0.45 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.09 mmol). After the mixture was stirred for 12 h at room temperature, reaction solution was added saturated aqueous NaHCO<sub>3</sub> (50 mL), and

extracted with diethyl ether (50 mL  $\times$  2). The extract was dried over MgSO<sub>4</sub> and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) and recrystallized from hexane to afford the ester ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I** as yellow crystals (yield 60–70%).

( $\pm$ )-**8-I**: IR  $\nu$  (KBr): 2936, 2853, 1736, 1508, 1261, 1202, 1171, 1005, 748, 600 cm<sup>-1</sup>; HRMS: Calcd. for C<sub>33</sub>H<sub>39</sub>INO<sub>4</sub> [M]<sup>+</sup>: 640.1924, Found 640.1922; Anal. Calcd. for C<sub>33</sub>H<sub>39</sub>INO<sub>4</sub>: C, 61.88; H, 6.14; N, 2.19. Found: C, 61.88; H, 6.24; N, 2.14.

( $\pm$ )-**12-I**: IR  $\nu$  (KBr): 2920, 2851, 1734, 1508, 1248, 1175, 1076, 1007, 743, 586 cm<sup>-1</sup>; HRMS: Calcd. for C<sub>37</sub>H<sub>47</sub>INO<sub>4</sub> [M]<sup>+</sup>: 696.2550, Found 696.2549; Anal. Calcd. for C<sub>37</sub>H<sub>47</sub>INO<sub>4</sub>: C, 63.79; H, 6.80; N, 2.01. Found: C, 64.04; H, 6.65; N, 1.98.

### 2.2. Determination of phase transition behaviors

The phase transition behaviors of ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I** are characterized by DSC analyses, polarized optical microscopy and variable temperature XRD analyses. For DSC analyses, each powder sample of 2–3 mg was put into an aluminum sample pan. Each sample was heated to 130 °C and cooled to room temperature at a rate of 5 °C/min under a flow of N<sub>2</sub> gas. For polarized optical microscopy, each sample was introduced by capillary action into an about 10- $\mu$ m thick handmade glass sandwich cell in which the inner surfaces of the two glass substrates were untreated. For XRD analyses, line profiles were recorded in the first heating and cooling processes.

### 2.3. Evaluation of magnetic properties

The temperature dependence of molar magnetic susceptibility measured on a SQUID magnetometer at a field of 0.5 T in the temperature range of 2–300 K in the first heating process. Each sample was enclosed in a DSC aluminum pan to prevent the sign inversion of the total magnetic susceptibility of samples in high temperature ranges.

The X-band EPR spectra were measured under an applied magnetic field of 0.33 T. Their *g* values and hyperfine coupling constants (*a<sub>N</sub>*) were determined by the measurements of THF solutions at room temperature. For the evaluation of paramagnetic susceptibility, four measurements of each powder and melt samples were performed at each temperature. Each sample was sealed in a quartz tube. Sweep time was 90 s, modulation width was 0.2 mT and time constant was 0.03 s.

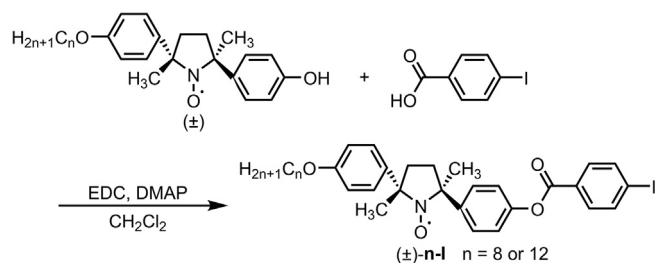
### 2.4. Determination of the crystal structure of ( $\pm$ )-**8-I**

Crystals of ( $\pm$ )-**8-I** suitable for XRD studies were prepared by recrystallization from hexane, and analyzed using an X-ray diffractometer. The X-ray crystal structure of ( $\pm$ )-**8-I** was solved by direct methods and refined using the full-matrix least-squares method. In subsequent refinements, the function  $\sum \omega(F_o^2 - F_c^2)^2$  was minimized, where *F<sub>o</sub>* and *F<sub>c</sub>* are the observed and calculated structure factor amplitudes, respectively. The positions of non-hydrogen atoms were determined from difference Fourier electron-density maps and refined anisotropically. All calculations were performed with the Crystal Structure crystallographic software package.

## 3. Results and discussion

### 3.1. Phase transition behavior

The phase transition behaviors of ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I** are characterized by DSC analyses at a scanning rate of 5 °C/min upon heating and cooling processes as shown in Fig. 1 and by polarized



Scheme 1. Synthesis and molecular structures of ( $\pm$ )-**8-I** and ( $\pm$ )-**12-I**.

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